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**Nepheline solid solution compositions: stoichiometry revisited, reviewed, clarified and rationalised.**

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**Supplementary file**

**S.1. Introduction.**

The compositions of natural nephelines are conventionally reported as wt. % oxides and most authors now calculate atomic proportions of cations on a 32 oxygen basis equivalent to the unit cell composition which contains 8 formula units of the fundamental nepheline end-member NaAlSiO4 (Ne). However, over the years some authors have reported the proportions of chosen end-member mineral molecules on a wt.% basis while others have used mole % values for such molecules, but commonly the reported method used is not specified.

Experimentally determined phase diagrams are conventionally used to display liquidus isotherms, crystal – silicate liquid field boundaries, and equilibrium coexisting mineral tie lines; such phase diagrams are always determined and discussed as wt.% systems and this is perhaps why many igneous petrologists reported phase analyses using wt.% end-member mineral proportions. In particular much attention was paid to determining the magmatic and sub-solidus phase stabilities of silica minerals, feldspars and feldspathoids in silica-saturated and silica-undersaturated bulk compositions with the stability relations in the quartz (Qz, SiO2) – nepheline (Ne, NaAlSiO4) – kalsilite (KAlSiO4) system displayed in the so-called Petrogeny’s Residua System (PRS, Schairer and Bowen, 1935).

With the advent of the electron microprobe, analyses of coexisting feldspars and feldspathoids in magmatic rocks became more common and authors continued to report compositions as wt.% or mole.% proportions of end-member minerals and plotted these data in the wt.% Qz – Ne – Ks (PRS) phase and the Hamilton diagram. Reporting the wt. % of end-member mineral molecules is an unambiguous procedure but differences emerge when recalculating mole % proportions of these molecules which results in different values being obtained by different authors for similar composition nephelines. Although different sets of data have been re-calculated on a mole % basis it is clear that different calculation procedures have been used whereby one method might have followed the strict rules of nepheline stoichiometry and structure while others did not.

In this paper I return to first principals in an attempt decipher the different calculation procedures that have been used and to develop a standardised, rigorous and logical way of dealing with this problem.

**S.2. Stoichiometry and composition review and background to a new approach**

Early chemical analyses of nepheline date back to the early 19th century and by the early 20th century many analyses had appeared which had been obtained by classical ‘wet’ methods on mineral separates obtained from coarse grained, silica-undersaturated rocks involving removal of impurity grains by hand-picking if necessary. In a key paper, Bannister and Hey (1931) gave 9 new analyses, 6 from Mt Somma, Vesuvius, which involved use of micro-analytical techniques with as little as 64.1 mg for one sample. Before the crystal structure had been determined using single-crystal X-ray diffraction techniques, Bannister and Hey (1931) combined their chemical analyses, densities, optical properties, and unit cell dimensions to deduce that the unit cell atomic formulae should be calculated to 32 oxygen atoms. On that basis they found that Si+Al averaged 15.995, consistent with 16 framework cations per unit cell, and with the number of Al atoms matching the sum (2Ca+Na+K). They also calculated 32 oxygen atomic formulae for about 100 nepheline analyses published over the previous 130 years and found a mean Si+Al of 15.995 and a value for (2Ca+Na+K) - Al of 0.02. Thus, they proposed that the unit cell contents could be given as Si(16–*n*)Al*n*(Na,K,Ca)nO32. For all of these data the average Si/Al averaged 1.10 showing that natural nepheline is consistently more siliceous than the (Na,K)AlSiO4 composition with about 10 atom % of excess Si. Note that many authors have also pointed this out and Bowen (1912) reported a mean formula of (Na,K)8Al8Si9O34 which is equivalent to the presence of 10 mol.% excess silica; Bowen was the first to attribute this to the solid solution of albite (NaAlSi3O8) in nepheline. Greig and Barth (1938) subsequently determined that the limit of solid solution of albite in Na nepheline at 1 bar pressure dry is ~ 33 wt.% (Ne67Ab33, wt.%) which is equivalent to Ne85Qz15 (wt.) and Ne83Qz17 (mol.). Edgar (1964) reported a solid solution composition limit of Ne75Ab25 (wt.%) at 835°C and 1000 bars *P*H2O.

The literature survey of nepheline compositions in Bannister and Hey (1931) commonly shows the presence of a significant Ca component whereas their new nepheline analyses showed a range of CaO from 1.99 to 2.51 wt.% (~ 10 - 12.5 wt.% An). Note this range does not include values for their analyses X and V (4.44 and 3.7, respectively) which Hey (pers. com., 1972) suggested might be incorrect (Henderson and Gibb, 1972). Bowen (1912b) had earlier determined experimentally at 1 bar that the maximum amount of solid solution of An in nepheline is ~ 35 wt.% (Ne65An35 and ~ 7 wt.% CaO) equivalent to Ne65.5An34.5 (molar). Although the natural mineral lisetite (Smith *et al.*, 1986) has the composition Ca0.98Na1.96Al3.99Si4.02O16 (9.8 wt.% CaO, 10.8 wt.% Na2O) with a nepheline/anorthite type stoichiometry it has a feldspar-type structure with 4-rings of tetrahedra ((Rossi *et al.*, 1986).

Melluso *et al.* (1996) used microprobe techniques to analyse feldspathoid groundmass phases in volcanic rocks from Mt Vulture, Italy, including nepheline and haüyne; CaO contents for nepheline in most samples were in the range 0.4 to 4.0 wt.% ( 2 – 20 wt.% An), within the range of equilibrium nephelines (Bowen, 1912b). However, one analysis showed 8.8 wt.% CaO, outside the probable stable nepheline compositional range, and also has major stoichiometry discrepancies with Al >> (Na+K+Ca) and substantial deficiencies in Si. It is possible that this groundmass spot-analysis was of an intergrowth of nepheline, haüyne and perhaps other Ca-rich phases including cancrinite. Experimental studies (Goldsmith, 1949) showed for the system NaAlSiO4 – CaO.Al2O3 at 1 bar could form nepheline solid solutions with at least 60 wt.% of CaAl2O4 but there is little evidence that natural nephelines could have Ca present as that molecule.

Subsequently, Donnay *et al.* (1959) used powder XRD methods to assess changes in hexagonal unit cell parameters in 4 series of synthetic nepheline-structured solid solution series: Ne – Ks, Ne – Ab, Ne – An, and Ne – CaAl2O4. Note that solid solutions in the Ne-Ab series and in the Ne-An series will both have cavity cation site vacancies reflecting the substitution of Si for Al in the former and of Ca for Na in the latter. For the Ne – Ks series they showed that the cell parameters versus composition graphs show distinct changes of slope at Ks contents of 25% (atomic) confirming the findings of Smith and Sahama (1954). Donnay *et al.* (1959) also suggested that any Fe3+ present substitutes for Si and Al in tetrahedral coordination, whereas the small amounts of Mg, Mn and Ti that might be present would substitute for Na, K, or Ca. Shortly after the Donnay paper, Hamilton (1961) and Hamilton and MacKenzie (1960) reported results for the experimental determination of nepheline compositions in Petrogeny’s Residua System at 1 kbar *P*H2O as a function of temperature and defined limits of solid solution of albite in nepheline for isotherms at 500, 700 and 775°. Plots of two-theta angles for 20.2 and 21.0 peaks versus composition showed changes of slope at Ne73.5Ks22.5Qz4.0 (wt.%) with a similar K/Na ratio to those found for binary Ne – Ks compositions. This ternary composition was also given as Ne71.24Ks19.59Qz9.37 (molecular %) and Na5.97Ks1.64□0.39Al7.51Si8.39O32 (Hamilton and MacKenzie, 1960). Note the much higher molecular % content of Qz compared to the equivalent wt.% value; it is clear that a molecular weight of 60 for Si was used to convert weight to molecular amounts for the excess Q component and this protocol is the same as that used by Dollase and Thomas (1983). However, on the basis of the Q’ component having a molecular weight of 120 (Si2O4), this Hamilton and MacKenzie composition would be Ne75.7Ks20.5Qz4.8 (molecular %). Hamilton and MacKenzie (1960) drew the join from Na6K2Al8Si8O32 to a point at 40% of the Q component which is labelled Na6□2Al8Si10O32 on the Na8Al8Si8O32 (8Ne) – 8SiO2 join on a version of the Ne–Ks–Q system; note that the Q corner has 8 Si atoms matching the Si content of the Na and K-component corners. The number of oxygens of the Q corner is half of that defined for a 32 oxygen unit cell and thus excess Q solid solutions do not match strict nepheline stoichiometry. Indeed the geometric position labelled Na6□2Al8Si8O32 by Hamilton and MacKenzie has the formula Na4.8□1.6Al4.8Si8O25.6 which is equivalent to 0.8 Na6□2Al8Si10O32. Dollase and Thomas (1978) also discuss the join Na6K2Al8Si8O32 – Na6□2Al8Si10O32 and show it on the system NaAlSiO4 – KAlSiO4 – SiO2 (mole %) without labelling the end points of the join. The number of oxygens for the Q corner is again half of those defining the Na and K end-members and the terminations of the join in this diagram are actually Na0.75K0.25AlSiO4 (shown at 25% of Ks) and Na0.6□0.2Al0.6Si1.0O3.2 (shown at 40% of Q); these formulae are equivalent to 0.125 Na6K2Al8Si8O32 and to 0.1 Na6□2Al8Si10O32 . Henderson and Gibb (1983) and Wilkinson and Hensel (1994) followed Dollase and Thomas in plotting the ‘join’ in a NaAlSiO4 – KAlSiO4 – SiO2 (mole %) triangle but incorrectly label the ends of this join on a 32 oxygen basis. It is clear that the correct way of displaying strict nepheline stoichiometry is to define each of the end-members on a 32 oxygen basis, i.e. Na8Al8Si8O32 – K8Al8Si8O32 – □8Si16O32; in that case the composition Na6□2Al8Si10O32 would plot at 75% and 25% of the Na- and Si- end-members of the join rather than the 60% and 40% proportions implied by Henderson and Gibb (1983). These differences result from the Q component having half the number of oxygens required for strict nepheline stoichiometry.

It is clear that natural nephelines crystallize with hexagonal symmetry (*P*63 space group) and that they have stuffed-tridymite structures with linked, staggered 6-membered rings of ordered Si, Al(Fe) tetrahedra with the Na, K, Ca and associated vacancies occupying the cavity cation sites with are defined by the holes in the polyhedral framework. All natural nephelines have two distinct cation sites with Na and Ca tending to occupy the smaller, and K and vacancies (□) the larger sites (e.g., Hahn and Buerger, 1955; Dollase, 1970). The presence of iron as Fe3+ substituting for Al in the tetrahedral sites is well established in framework silicates and is usually found in chemical and microprobe analyses of nepheline. However, wet chemical analyses of nepheline separates sometimes contain very small amounts of Mg, Fe2+, Mn and Ti although these components most probably result from the presence of grain impurities and/or alteration products (Dollase and Thomas, 1978). However, synthetic leucite analogues are known to contain large amounts of divalent cations (e.g., Mg, Zn, Co, Fe2+, Cd) in the polymerized framework of general formulae K2M2+Si4+5O12 (e.g, Roedder,1951; Martinez and West, 1986; Henderson *et al.*, 1998, 2017) involving the coupled substitution 2Al3+ → M2+ + Si4+. Thus, it is relevant that Roedder reported the synthesis of hexagonal nepheline-like phases of composition K2[MgSi3O8] (Roedder, 1951) and K2[Fe2+Si3O8] (Roedder, 1952; also see Buerger, 1954). Other ‘exotic’ synthetic silicate phases also have stuffed-tridymite nepheline structures with linked 6-rings of tetrahedra which contain divalent cations and Si in separate sites, e.g. Ba*M*SiO4 with *M* = Co, Zn, Mg (Liu and Barbier, 1993). It is clear that inclusions and composite grains can be avoided using the electron microprobe (Dollase and Thomas, 1978) and, if found using high-quality microprobe analysis, it is possible that small contents of Mg, Mn and Ti occupy the nepheline framework and that all Ca replaces Na in the cavity sites. Note that complete solid solutions in the system SrAl2O4 – BaAl2O4 show that Sr and Ba occupy cavity sites in kalsilite-like structures which have stuffed tridymite topology (Henderson and Taylor, 1982). These assumptions will be followed in the following sections where we will refer to the calcic molecule as Ca-Ne (calcium-Ne, formula □Ca0.5Ca0.5AlSiO4) rather than An’ (Barth, 1963) and total excess silica as Q’ (□SiSi2O4) (Barth, 1963).

**S.3. Assessment of igneous rock nepheline compositions.**

The conventional method for calculating the end-member components Ne, Ks and An and Qz as weight proportions is straightforward by multiplying the wt.% Na2O, K2O and CaO by 284.11/61.98, 316.32/94.20, and 278.21/56.08, respectively; the excess Si amount (Sixs) is provided by subtracting the wt.% SiO2 contained in those amounts of Ne, Ks and Qz from the total analysed wt.% SiO2 and recalculating to 100% if necessary. Alternatively Qxs (wt.%) = total wt.% SiO2 wt.% Na2O x 120.18/61.98 wt.% K2O x 120.18/94.2 wt.% CaO x 120.18/56.08.

Based on recalculation of nepheline analyses to a 32 oxygen nepheline unit cell, Bannister and Hey (1931) pointed out that nepheline compositions should have a valence sum for cavity cations closely balanced by the number of tetrahedral trivalent cations; the samples studied showed that 2Ca + Na + K was in excess of the total Al + Fe3+ by an average of ~ 0.02 (range –0.7 to +0.52). In their data (their Table 2) 4 of the 9 samples showed an excess of cavity cations whereas the published analyses discussed by them (their Table 4) 34 of 66 analyses showed an excess of cavity cations. Clearly an excess positive cavity cation charge over that for the sum of trivalent tetrahedral Al commonly occurs. Bannister and Hey pointed out “The number of oxygen atoms associated with a monovalent term is ½, a divalent term 1 &c.” , and this reasoning is completed here by defining 3/2 oxygens for Al and 2 for Si; they also showed that this difference is four times larger than the difference 16 - (Si + Al). This is arithmetically correct but is not related to nepheline stoichiometry; it simply reflects the fact that the input oxide components and 32 oxygen atomic formula units are both electrostatically balanced; indeed non-stoichiometric ‘nepheline’ atomic proportions show the same 1:4 relation mentioned above. If there is an excess of cavity cation charges over the total trivalent tetrahedral cation sum, the positive charge from the excess Na+ could be balanced by Si-O components of the framework although this would imply disruption of some Si – O – O linkages in the framework. Such Na-O-Si linkages could be similar to those occurring in beta sodium disilicate (β-Na2Si2O5); this compound exists as the natural mineral natrosilite which is a monoclinic, pseudo-hexagonal sheet-like compound with the sheets containing six-rings of SiO44- alternating with layers of 5- or 6-coordinated Na-O polyhedra (Pant, 1968; Kahlenberg, 2010). However, is is more probable that the charge on any excess alkali content could be neutralised by the presence of large anions (e.g., CO32-, Cl) as in cancrinites (see below).

In a subsequent key paper Dollase and Thomas (1978) reassessed the Bannister and Hey criteria and concluded that the difference between 2Ca + Na + K and Al + Fe3+ (or the difference between total valence sum for tetrahedral cations and the ‘ideal’ value for 16 x mean tetrahedral cation valence) should fall within ±0.25 atoms per 32 oxygens for acceptable analyses. To assess these chemical controls in more detail in this paper a ∆(Al-cavity cations, ∆Alcc) parameter is calculated for tetrahedral (Al+Fe3+) – cavity cations (Na+K+2Ca) (atoms per 32 O unit cell), and a ∆(tetrahedral charge, ∆Tcharge) parameter as [{(Al+Fe3+) x 3 + (Si+Ti) x4} – {16 x mean tetrahedral charge calculated for the sample}]. For the analyses given by Bannister and Hey (their Table 1) the former would have a mean value -0.011 (range

-0.678 to +0.517), and the latter a mean value of –0.017 (range –0.608 to +0.456). The average ∆Alcc/∆Tcharge ratio for their samples is 1.17 (range 1.01 to 1.24). The ∆Alcc/∆Tcharge ratio must reflect a Si/Al ratio > 1 as expected for natural nephelines. For **strict** nepheline stoichiometry (unit cell 32 oxygens, 16 T atoms, 8 cavity sites, Si = Al) ∆Alcc = 0 and ∆Tcharge = 0. For departures from these ‘ideal’ values, delta parameters would be coupled with either positive or negative values but both should have the same sign and have similar values in the absence of significant analytical errors. Based on the formulation used to define the delta values, an increase of the T site cation total to > 16.00 would lead to negative ∆Tcharge values (coupled to negative ∆Alcc) and if the T cation site total is < 16.00 the ∆Tcharge would be positive (*cf.* +ve ∆Alcc).

The fact that natural nephelines mostly have Si/Al ratios >1.0 has been accounted for by the presence of a feldspar-like component (e.g, NaAlSi3O8) and the same could be said for an anhydrous analcime component (NaAlSi2O6); such solid solutions would of course have stuffed tridymite frameworks (see above). Using ‘nepheline’ 32 oxygen unit cell stoichiometry, ∆Alcc and ∆Tcharge parameters for ideal NaAlSiO4, NaAlSi2O6 and NaAlSi3O8 should have zero values for both delta parameters for these three end-members with the different Si/Al ratios of 1, 2 and 3, respectively. By allowing a very small degree of non-stoichiometry for the Si, Al or Na components, the ∆Alcc /∆Tcharge ratios are close to 1.07, 1.09 and 1.14, respectively (Table S.1) and analyses of natural minerals confirm these ∆Alcc /∆Tcharge ratios (Table S.1); note that the size of the delta values relative to zero reflects their departure from ideal nepheline stoichiometry. Thus, compositional variation within natural nephelines would be expected to show at least this range of ∆Alcc /∆Tcharge ratios for acceptable nepheline analyses. Note that other framework-structured minerals show similar types of coupled ∆Alcc and ∆Tcharge relationships with cancrinite- and sodalite-group minerals having essentially the same ratios as ideal nephelines reflecting their structural and chemical similarities to nephelines while zeolites have delta ratios close to feldspars than to nephelines. All of these phases are commonly associated with natural nephelines, often as sub-solidus alteration products.

**Table S.1.** 32 oxygen-based delta values for ideal and natural framework minerals

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Table / Column | ∆Alcc | ∆T charge | ∆Alcc/∆Tcharge |
| *Ideal* |  |  |  |  |
| NaAlSiO4 |  | 0.00019 | 0.00017 | 1.143 |
| NaAlSi2O6.H2O |  | 0.00014 | 0.00013 | 1.091 |
| NaAlSi3O8 |  | 0.00074 | 0.00064 | 1.067 |
|  |  |  |  |  |
| *Natural* |  |  |  |  |
| Nepheline | 35 / 1 | –0.28 | –0.24 | 1.130 |
| Analcime | 40 / 1 | 0.370 | 0.337 | 1.097 |
| Leucite | 36 / 1 | –0.012 | –0.011 | 1.093 |
| Amelia albite | Web | –0.0075 | –0.0071 | 1.068 |
| Alk. feld. Na/K | 30 / 9 | 0.094 | 0.085 | 1.066 |
| Vishnevite | 38 / 2 | –3.43 | –3.00 | 1.141 |
| Microsommite | 38 / 3 | –5.72 | –5.00 | 1.142 |
| Sodalite | 37 / 1 | –2.90 | –2.54 | 1.144 |
| Hauyne | 37 / 6 | –3.19 | 2.80 | 1.139 |
| Natrolite | 42 / 1 | 0.39 | 0.35 | 1.112 |
| Mesolite\* | 62 / 7 | –0.11 | –0.10 | 1.105 |
| Phillipsite | 42 / 9 | –0.059 | –0.053 | 1.101 |

\* Source Deer *et al.* (2004); others from Deer *et al.* (1966)

**S.4. Further criteria for assessing reliability of nepheline analyses.**

In this section the criteria for using the ∆Alcc (Bannister and Hey, 1931; Dollase and Thomas. 1978) and ∆Tcharge (Dollase and Thomas, 1978) parameters are assessed together with a new one based on the present calculation system, namely ∆(Qxs – QSi) which reflects departures from **ideal** nepheline stoichiometry. Based on the formulae given in Table 2, four different delta values based on numbers of atoms per 32 oxygens can be defined:

∆(Qxs – QSi) = [24/24 – 3Na/24 – 3K/24 – 6Ca/24] – [Sitotal/16 – Na/16 – K/16 – 2Ca/16]

which simplifies to ∆(Qxs – Qsi) = 16 – Na – K – 2Ca - Sitotal.

∆(Qxs – Qcav) = [24/24 – 3Na/24 – 3K/24 – 6Ca/24] – [24/8 – Sitotal/8 – (Al+Fe3+)/8 – Na/8 – K/8 – 2Ca/8]

which simplifies to ∆(Qxs – Qcav) = Sitotal + (Al+Fe3+) – 16

∆(QSi – Qcav) = [Sitotal/16 – Na/16 – K/16 – 2Ca/16] – [24/8 – Sitotal/8 – (Al+Fe3+)/8 – Na/8 – K/8 – 2Ca/8]

which simplifies to ∆(QSi – Qcav) = 3Sitot + 2(Al+Fe3+) + 2Ca +Na + K - 48.

a∆(Qxs – Q(Si-Al)) = [24/24 – 3Na/24 – 3K/24 – 6Ca/24] – [Sitotal/16 – (Al+Fe3+)/16]

which simplifies to ∆(Qxs – Q(Si-Al)) = 16 – 2Na – 2K – 4Ca – Sitotal + (Al + Fe3+)

For ideal nepheline stoichiometry (Al+Fe3+) = (Na + K + 2Ca) so all of these equations are identical and reduce to ∆Q’ = 16 – Sitotal – Al, but analytical errors and degree of non-stoichiometry differences combine to give each ∆Q’ a different value. The scales of the ∆(Qxs – QSi) and ∆(Qxs – Q(Si-Al)) departures from 0 are not affected by the Al+Fe term, ∆(Qxs – Qcav) is only affected by departure of framework cations from 16, and ∆(QSi – Qcav) is affected by all chemical components. The Qxs value is used here to define the preferred excess Si component as that is closest to the system reported by Barth (1963).

**S.5. Excel spread sheets.**

Two spread sheets are provided for researchers to follow how the various parameters described in the main paper were calculated. The representative nepheline compositions chosen from different parent rock types shown in Table 4 of the main paper are used in these files. The working equations in the spreadsheet are locked but the input data columns are open so that users can substitute their own wt.% analytical data to obtain the atomic/molecular parameters they require. The formulae are not hidden which will aid understanding.

Table S.3 provides the means of calculating parameters using the total analysed Na content to calculated the appropriate Ne end members. For nephelines from highly peralkaline rocks the main paper shows that those generally have excess alkali cations over the Al and Fe3+ proportions which leads to Ne vales too large and usually to unreliable excess Q contents. Table S.4 provides a mean of correcting for this by calculating the excess Si from total Si minus atoms of Al and Fe3+ as described in the main paper. Thus a Na value matching the value (Al+Fe3+) is taken as the correct stoichiometric amount of Na in the nepheline analysis and the excess Na is obtained by subtracting that from the total Na. The Naxs value is not part of the nepheline component and can be used to estimate a separate Na-cancrinite component (see main paper). The new nepheline oxygen components no longer sum to 32 and must be recalculated to 32 O as done within the spreadsheet.

*Table S.3. Calculation using total analysed Na content*.

Note that the highlighted columns are most useful in assessing the nepheline compositions.

The column contents are described as follows.

A-B give sample information.

D-Q give wt.% oxide data for the various components together with an analytical total

S has the factor used to calculate the analytical data to atoms of cations per 32 O

U – AG gives numbers of cations per 32 O

AI is Si/Al (atomic)

AJ – AL various parameters

AM ∆(Al+Fe3+) – cavity cations’ ∆Alcc

AN gives ∆Tcharge

AO ∆Alcc / ∆Tcharge

AP define proportion of excess Si from Eqn 1 (Table 2 main paper)

AS - AY various parameters with AY = ∆Tcharge

BA Sixs1 Eqn 1

BB cavity cation vacancies

BC mole % total Ne Eqn 4

BD aluminium Ne

BE Fe3+ iron Ne

BF Ks, Eqn 5

BG Ca nepheline CaNe Eqn 6

BH K2*M2+*Ks Eqn 14

BL – BP various excess Q values

BL Qxs Eqn 3

BM QSi Eqn 7

BN Qcavity cation Eqn 10

BO Qcavity cation Eqn 9

BP Q(Si-Al) Eqn 8

BR Delta (Qxs – QSi) x 24 / 100

BS Delta (Qxs – QSi) / Qxs

BU – BW % Ne, Ks, Qxs recalculated to 100%

BX – CB Ne, Ks, CaNe, Qcavity. Q(Si-Al) calculated to 8 cavity cations using Eqns 11, 12,13 and 8, respectively.

CD-CF Ne, Ks and Qcavity proportions recalculated to 100%

CH – CI Ne, Ks, Q(Si-Al) proportions recalculated to 100%

Note that the different Q’ values show significant differences which show departures from strict stiffed-tridymite stoichiometry

*Table S.4. Dealing with nephelines from highly peralkaline rocks.*

Note that the highlighted columns are most useful in assessing the nepheline compositions.

The column contents are described as follows.

A-B give sample information.

D-Q give wt.% oxide data for the various components together with an analytical total

S has the factor used to calculate the analytical data to atoms of cations per 32 O

U – AG gives numbers of cations per 32 O

AI Corrected Na (8 - K – 2Ca – [(Si-Al)/2] See main text

AJ Naxs (Total Na – corrected Na)

AL – AN defining values required to recalc O to 32

AP – AW new atomic proportions per 32 O

AY - BB sums of all cations, sum cavity cations, sum T cations, vacancies in cavity site

BD excess Sixs, Eqn 2

BE – BF required to calculate ∆Tcharge

BH ∆Acc

BI ∆Tcharge

BK Si / Al

BL ∆Acc / ∆Tcharge

BP Sixs Eqn 1

BQ excess Q Qxs % Eqn 7

BS – BV Calculation of ∆Tcharge

BX – CD Mol proportions of Ne total, NeAl, NeFe3+, Ks, CaNe, K2M2+Ks

CE Sixs1 Eqn 1

CF cation deficiencies in the cavity site

CH % Na-cancrinite (see main text)

CI % Ne (corrected)

CJ – CK % Al Ne and Fe3+Ne

CL % Ks, Eqn 5,

CM %CaNe, Eqn 6

CN % K2M2+Ks, Eqn 14

CQ - CT Q’ parameters: Qxs Eqn 3, Qsi Eqn 7, Qcavity Eqn 9, and Q(Si-Al) Eqn 8.

CV – CX Ne, Ks, Qxs recalculated to 100%.

Note that the different Q values are now very similar showing that making the Na correction eliminates most of the apparent non-stoichiometry.

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