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Occurrence and properties of lisetite, $CaNa_2Al_4Si_4O_{16}$, a new tectosilicate in the system Ca-Na-Al-Si-O

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ABSTRACT

Lisetite occurs in strongly retrograded clinopyroxene-rich layers in the Liset eclogite pod in the Selje district of the Western Gneiss region, Norway.

Electron-microprobe analyses reveal the almost stoichiometric composition $CaNa_2Al_4Si_4O_{16}$, which is chemically identical to exactly 50% anorthite ($Ca_2Al_4Si_4O_{16}$) + 50% of the pure-Na equivalent of nepheline ($Na_4Al_4Si_4O_{16}$). The mineral is a tectosilicate with all Al in tetrahedral sites, but it is neither a feldspar nor a feldspathoid. The crystal structure is orthorhombic with space group $Pbc2_1$ and unit-cell parameters $a = 8.260(1)$, $b = 17.086(1)$, $c = 9.654(1)$ Å, $V = 1362.5(4)$ Å^3, $Z = 4$, $D_{calc} = 2.73$. The strongest X-ray powder-diffraction reflections are [d in Å, (I/I_0), (hkl)] 3.198(100)(042,231); 4.162(44)(200); 3.468(36)(221); 3.534(31)(141); and 2.954(31)(113).

In the type thin section, lisetite is anhedral, untwinned, uncleaved, transparent, and colorless with refractive indices and birefringence similar to those of plagioclase. Lisetite, which occurs in clusters of ~100-μm-sized grains, is however easily distinguished from the abundant plagioclase in the type sample by its rich collection of micrometer-sized mineral inclusions and by a characteristic double corona texture. This corona includes a zone of a new K-poor, Ca-rich nepheline-structure mineral.

Very localized diffusion of principally the ions Na^+, Ca^{2+}, and H^+, related essentially to the destabilization of jadeite-rich clinopyroxene, can explain the main features in the sequence of mineral development in this rock. Lisetite grew via intermediate reactions involving paragonite, and perhaps also corundum + albite, in Al-rich Si-poor domains originally represented by eclogite-facies kyanite. The stability field of lisetite is approximately estimated to lie between 10 ± 4 kbar at 400°C and 20 ± 4 kbar at 800°C where highest-pressure greenschist-, amphibolite-, or granulite-facies parageneses form.

INTRODUCTION

Old and new minerals in the chemical system Ca-Na-Al-Si-O

This simple chemical system is represented in nature by several very common minerals including feldspars and, if K is also present, feldspathoids that together constitute a major part of the tectosilicate mineral class. A vast amount of experimental work at low to high pressures (P) and temperatures (T) has been carried out over the years by many workers in order to map out in P-T space the stability fields of these tectosilicates and the reaction curves by which they may be transformed into more dense mineral species containing octahedral rather than tetrahedral Al (e.g., jadeite or grossular). In this context it is interesting to find only now a new mineral that lies chemically in the middle of the system and petrologically in intermediate metamorphic P-T conditions. In this article we present the essential description of the new mineral lisetite along with some brief petrologic notes concerning its peculiar occurrence, which is intimately related to that of a second new mineral in the same chemical system: a K-poor, Ca-rich mineral with the nepheline framework (Smith, 1984a; Rossi et al., 1985). The crystal structure of lisetite and its relation to other tectosilicates are described in Rossi et al. (1986).

Type sample

The co-type crystal (no. LT2), whose structure has been refined by single-crystal X-ray diffractometry, occurs in rock sample no. G201b and is deposited in the Museum of the Dipartimento di Scienze della Terra, Università di Pavia, Italy. Several other crystals from the same polycrystalline cluster, including the co-type crystal (no. LT1), are still in thin section no. G201b7, which is deposited in the Galerie de Minéralogie, Muséum National d'Histoire Naturelle, Paris, France.

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The mineral name is for the locality, and its recognition was approved by the IMA Commission on New Minerals and Mineral Names in 1985 (no. 85-17).

OCCURRENCE

Mineral and chemical context at Liset

The ~60-m-long and ~30-m-wide compositionally layered Liset eclogite pod differs in many respects from all other known eclogite pods enclosed within gneiss in the Western Gneiss region of S.W. Norway. For example, its bulk-rock chemistry is unusually Na- and Al-rich and K- and Mg-poor (Smith, 1976; Kechid, 1984), and several of its complex microtextures (numerous types of retrograde symplectites and coronas) and internal macrostructures (many small pods within a larger pod) are quite atypical (Kechid and Smith, 1982; Kechid, 1984). Most of all, its mineral chemistry is unmatched; this is due partly to the locally extreme bulk-rock chemistry and partly to the high *P* of formation of the eclogite-facies parageneses. The apparently unique mineral compositions found to date in either the eclogite- or the posteclogite-facies assemblages include (1) F-rich nyböite (Smith and Lappin, 1982), (2) ferro-alumino-taramite (Smith and Lappin, 1982; Ungaretti et al., 1985), (3) the nearly pure Na equivalent of eastonite (Smith and Kechid, 1983), (4) both margarite and paragonite containing substantial solid solution toward the hypothetical endmember mica $Na_2(Mg,Fe^{2+})_1Al_4Si_4Al_4O_{20}(OH)_4$ (Smith and Kechid, 1983; Smith, 1984a), (5) both Mg-rich pyrophanite and Mn-rich geikielite (Pinet and Smith, 1985; Smith and Pinet, 1985), and (6) both of the new Ca-Na-Al-Si-O tectosilicates mentioned above.

The rather uncommon mineral compositions that occur include (1) omphacite and jadeite compositions ranging without a gap over the omphacite-jadeite solvus (Smith and Lappin, 1982; Kechid, 1984; cf. Carpenter and Smith, 1981), (2) Ca-poor almandine with as low as 7 mol% (grossular + andradite) (Kechid and Smith, 1985), (3) Al- and F-rich sphene (titanite) with up to 37 mol% of the Al endmember (Smith, 1980a), (4) Mg-rich staurolite with Mg/(Mg + Fe) up to 0.5 (Smith, 1984a), (5) magnesio-alumino-taramite (Kechid and Smith, 1982; Ungaretti et al., 1985), and (6) pure preiswerkite (Smith and Kechid, 1983). The minerals of relatively ordinary composition that occur include quartz, kyanite, corundum, plagioclase, aegirine and aegirine-augite, allanite, zoisite and/or clinozoisite, epidote, muscovite, eastonite, chlorite, rutile, ilmenite, hematite, magnetite, apatite, monazite, and diverse clinoamphiboles and sulphides (Kechid, 1984).

Petrologic context at Liset

In the whole Liset eclogite pod, numerous mineral assemblages in *apparent equilibrium* are displayed. Most of these can be assigned to one of two groups: (1) Al^{VI}-rich eclogite-facies parageneses (anhydrous or hydrous) and (2) Al^{IV}-rich amphibolite- or greenschist-facies parageneses formed from the first group. The textural data indicate that the lisetite developed between these two sets of facies such that the lisetite growth marks the earliest posteclogite stage of retrograde metamorphism. This stage has been attributed to a tectonic introduction of the eclogite pod into lower-*P* gneisses (Kechid and Smith, 1985; cf. the "lithospheric interdigitation" model of Smith, 1980b). Attention is drawn to the former coexistence of jadeite + quartz, which are often separated by only a narrow 100–200-μm-wide reaction rim composed of typical retrograde plagioclase + clinoamphibole. This mineral pair, along with coexisting paragonite + jadeite + kyanite, clearly indicates the very high *P* conditions (minimum $P = 17$ kbar) of the eclogite-facies stage of metamorphism in the Liset pod; other paragenetic data suggest intermediate *T* (650 ± 100°C) during the eclogite formation (Kechid, 1984; Kechid and Smith, 1985). Similar high-*P* conditions have been suggested for several other nearby eclogite pods, e.g., 17–29 kbar or even higher (Lappin and Smith, 1981). Although Liset lies only 1 km away from the first coesite-eclogite locality (Smith, 1984b) in the Norwegian coesite-eclogite province (Smith, 1985), the former presence of coesite at Liset has not (yet) been proved, despite some textural suggestions thereof (Kechid, 1984; Kechid and Smith, 1985).

Numerous mineral assemblages in *obvious disequilibrium* are also displayed. These include the coexistence in sample G201b9 of jadeite, quartz, albite, and the new K-poor, Ca-rich nepheline-structure mineral, as well as lisetite, all within 1 mm or less of each other (Fig. 1 shows all of these minerals except quartz). The relict jadeite is armored by a wide zone of cryptocrystalline symplectite, and the relict quartz is armored by a narrow but complete corona of aegirine-augite. The polycrystalline clusters of ~100-μm-diameter anhedral crystals of lisetite are almost always surrounded by a polycrystalline corona of the K-poor, Ca-rich nepheline-structure mineral, which is in turn almost always surrounded by a corona of magnesio-alumino-taramite (i.e., a double corona; Fig. 1). The whole lathlike assemblage is enveloped in the rock matrix comprising a medium-grained symplectite of albite + magnesio-alumino-taramite, which constitutes the amphibolite-facies paragenesis in this retrograded Na- and Al-rich, K- and Mg-poor eclogite pod. Occasionally the lisetite clusters are armored by a narrow opaque zone. All of the lisetite grains contain a large population of micrometer-sized crystalline inclusions, some of which have been identified as hematite, ilmenite, or högbomite; others may be of magnetite, corundum, plagioclase, amphibole, or mica (Fig. 1). These inclusions are believed to represent local concentrations of elements that were derived from the immediately preceding mineral assemblage (most probably including paragonite) but that cannot enter the lisetite tectosilicate structure, i.e., typical octahedrally coordinated atoms such as Mg, Fe, and Ti, as well as (OH).

CHEMICAL COMPOSITION

Table 1 gives the mean value and range of fifteen lisetite crystals analyzed with the Cameca CAMEBAX electron mi-

Fig. 1a. Typical lathlike texture of a lisetite cluster and its environment. The center is occupied by an irregularly shaped cluster of lisetite (white) full of micrometer-sized inclusions (gray and black). This is surrounded by an almost continuous polycrystalline corona of the K-poor, Ca-rich nepheline-structure mineral (white without inclusions) which in turn is surrounded by an almost continuous corona of joined magnesio-alumino-taramite crystals (dark) with occasional opaque minerals. This double corona is enveloped in a matrix of medium-grained albite (white) + magnesio-alumino-taramite (various grays) symplectite. At the right is a clear relict crystal of jadeite (almost white) corroded by a cryptocrystalline symplectite. Thin section no. G201b9. Parallel-polarized light. Field width = 2000 μm.

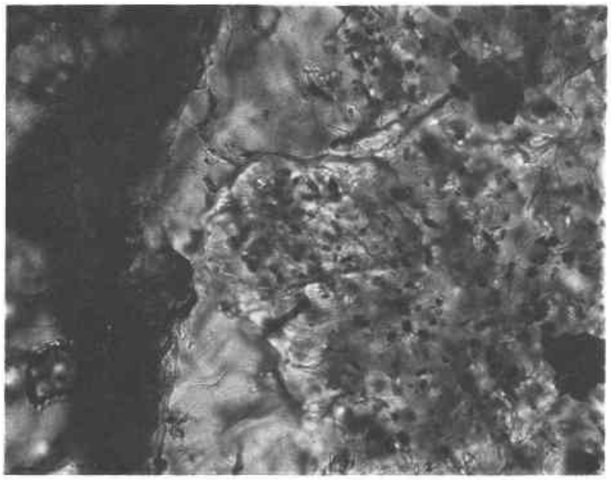

Fig. 1b. Enlargement showing the upper-left-central part of Fig. 1a. Note the clear zone of the nepheline-structure mineral separating the amphibole from the inclusion-rich lisetite (of higher relief) where opaque Fe-Ti oxides can be distinguished from almost colorless additional inclusions, probably including corundum, plagioclase, amphibole, or mica. Field width = 400 μm.

croprobe at the Muséum National d'Histoire Naturelle, Paris. The operating conditions were 15 kV and 12 nA with standard CAMEBAX ZAF corrections. The following standards were used: wollastonite (Ca, Si), corundum (Al), albite (Na), orthoclase (K), olivine (Mg), hematite (Fe), rhodonite (Mn), rutile (Ti), Cr_2O_3 (Cr), and NiO (Ni). No other elements were detected during a wavelength scan over all elements with atomic number greater than 10. The total weight percentage implies that no light elements are present in significant amounts.

The formula of the mean analysis on the basis of 16 oxygens is "Ca"$_{0.993}$"Na"$_{1.961}$"Al"$_{3.993}$"Si"$_{4.019}$$O_{16}$, where the minor elements are included as follows: Mg, Ni, Fe^{2+}, and Mn with "Ca"; K with "Na"; Cr with "Al"; and Ti with "Si." The range of variation is small enough to be accounted for by routine analytical uncertainty and/or by slight contamination due to the presence of the above-mentioned numerous micrometer-sized crystalline inclusions. These inclusions can adequately account for the trivial contents of Ti, Cr, Fe, Mn, Mg, Ni, and K in the analyses, especially since *all* these elements have a zero value in several of the individual spot analyses (Table 1). The analyzed Si/Al ratio = 1.006 and the Na/Ca ratio = 2.002; they are thus effectively identical to the ideal values, as is the (Al + Si) = 8.010 value. The small deficiency in (Ca + Na) = 2.939 may be adequately explained by a slight but real monovalent and/or divalent cation vacancy due to replacement of some trivalent Al by tetravalent Si (cf. the "edenitic" vacancy substitution: $Na^+ + Al^{3+} = \square + Si^{4+}$ in amphiboles), as is well known in nepheline. This (Ca + Na) deficiency has been confirmed by the crystal-structure refinement (Rossi et al., 1986). A slight alkali loss, as is common in electron-microprobe analyses of several mineral groups including alkali feldspars, may also have occurred. Hence all four factors are probably involved, but the differences between the full analysis given above, the trace-element-free formula ($Ca_{0.980}Na_{1.962}Al_{3.997}Si_{4.021}O_{16}$) (Table 1), and the ideal formula ($CaNa_2Al_4Si_4O_{16}$) are so small that these problems may henceforth be neglected.

Table 1. Mean and range of fifteen electron-microprobe analyses of lisetite

Oxides	Mean wt%	Min. wt%	Max. wt%		Cations per 16 oxygens		
					Mean	Mean*	Ideal
SiO_2	43.09	42.00	43.90	Si	4.017	4.021	4.000
TiO_2	0.02	0.00	0.14**	Ti	0.002		
Al_2O_3	36.33	35.89	36.70	Al	3.993	3.997	4.000
Cr_2O_3	0.00	0.00	0.03	Cr	0.000		
FeO	0.12	0.00	0.56**	Fe	0.010		
MnO	0.01	0.00	0.03	Mn	0.001		
MgO	0.01	0.00	0.02	Mg	0.001		
NiO	0.03	0.00	0.15**	Ni	0.002		
CaO	9.80	9.51	10.19	Ca	0.979	0.980	1.000
Na_2O	10.84	10.16	11.39	Na	1.960	1.962	2.000
K_2O	0.01	0.00	0.04	K	0.001		
Sum	100.26	98.85†	101.26‡		10.966	10.960	11.000

Note: Thirteen analyses from rock sample G201b and two from rock sample G209g, both from Liset.

* Excluding the seven trace elements Ti, Cr, Fe, Mn, Mg, Ni, and K and recalculating to O = 16.

** Much higher value than all the other fourteen values of this oxide; hence minor contamination reasonably certain.

† Corresponds to the lowest Na_2O value (i.e., Na loss ?).

‡ Corresponds to the highest FeO value (i.e., Fe contamination ?).

The composition of lisetite (recommended abbreviation: Lt) may thus be defined as stoichiometric $CaNa_2Al_4Si_4O_{16}$, i.e., chemically identical to exactly 50 mol% anorthite ($Ca_2Al_4Si_4O_{16}$) plus 50 mol% of the pure Na equivalent of nepheline ($Na_4Al_4Si_4O_{16}$). Lisetite is thus related to these two "endmember" compositions in the Ca-Na-Al-Si-O chemical system by the simple substitu-

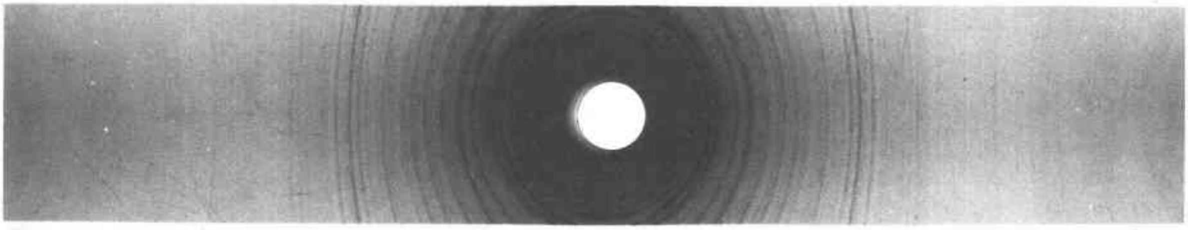

Fig. 2. A Gandolfi pattern of lisetite (camera radius 28.7 mm; Ni-filtered Cu radiation; crystal no. LT2).

tion $Na^+ + Na^+ = \square + Ca^{2+}$, as occurs between jadeite and Ca-Eskola's pyroxene and between richterite and tremolite, though in these pyroxene and amphibole analogies the mineral group remains the same. Lisetite thus has 11 cations per 16 oxygens whereas feldspars have 10 and feldspathoids have 12.

X-RAY CRYSTALLOGRAPHY AND PHYSICAL PROPERTIES

Lisetite is orthorhombic with space group $Pbc2_1$ as determined by single-crystal X-ray diffraction. The unit-cell parameters obtained during the course of the crystal-structure analysis (Rossi et al., 1986) are a = 8.260(1), b = 17.086(1), c = 9.654(1) Å, V = 1362.5(4) Å^3. The axial orientation has been chosen by taking into account the marked *Pbcn* pseudosymmetry.

Four $CaNa_2Al_4Si_4O_{16}$ formula units are contained in the unit cell and D_{calc} is 2.73. Sample scarcity and size prohibited a direct measurement of the density; such a measurement would in any case not be meaningful, given the substantial content of micrometer-sized inclusions in the lisetite at Liset (Fig. 1).

An X-ray powder-diffraction pattern was obtained with a Gandolfi camera (Fig. 2). The indexed Gandolfi pattern together with the pattern calculated from the single-crystal structure determination are presented in Table 2. The latter determination (Rossi et al., 1986) shows that lisetite is a tectosilicate whose tetrahedral framework is related to that of feldspars.

Neither cleavage nor twinning has been observed in lisetite, which is transparent, colorless, and anhedral. The birefringence is distinctly higher than that of the adjacent K-poor, Ca-rich nepheline-structure mineral but is essentially identical to that of nearby sodic plagioclase and quartz; hence $n_\gamma - n_\alpha = 0.009 \pm 0.001$. The refractive indices, which have not been measured directly owing to sample size and scarcity, are higher than those of the adjacent K-poor, Ca-rich nepheline-structure mineral (Fig. 1) and are estimated to be similar to those of calcic plagioclase, i.e., $n_\alpha = 1.56 \pm 0.02$, $n_\gamma = 1.57 \pm 0.02$.

DISCUSSION AND CONCLUSIONS

The creation and the breakdown of the lisetite at Liset will be discussed at length along with that of the neighboring K-poor, Ca-rich nepheline-structure mineral in a detailed petrographic description (Smith and Kechid, in prep.). A few petrologic points may, however, be of interest here since only rarely are new minerals found in the center of a well-known chemical system.

First, there exists strong textural evidence for the involvement of paragonite, or of its typical corundum + albite breakdown products, in the creation of lisetite (Kechid, 1984), but no direct textural evidence for the coexistence of lisetite with eclogite-facies parageneses. Lisetite development may thus be confidently attributed to one of the successive *retrograde* metamorphic events. Since there also exists some evidence for the growth of paragonite after kyanite (Kechid, 1984), then kyanite may have been responsible for the original high Al/Si ratio, and to some extent also for the frequent lathlike shapes, of the lisetite clusters.

Second, given (1) that Na^+ and Ca^{2+} influx and H^+ efflux are all that is necessary to transform paragonite into lis-

Table 2. X-ray powder-diffraction pattern of lisetite

*d** (Å)	I/I_0*	*hkl**	*d*** (Å)
7.468	8	110	7.42
5.906	11	111	5.90
4.162	44	200	4.14
3.754	11	122	3.74 (broad)
3.735	10	220, 211	
3.534	31	141	3.54
3.468	36	221	3.48
3.198	100	042, 231	3.19
3.155	18	150, 202	
3.100	21	212	3.09
3.010	15	023, 151	3.00 (broad)
2.988	12	142, 240	
2.954	31	113	2.94
2.759	10	232	2.75
2.540	11	251, 242	2.53
2.383	8	312	2.37
2.317	6	252, 322	2.31 (broad)
2.262	8	341	
2.186	7	243	2.20
2.146	6	134	
2.083	10	204, 400	2.09
1.979	6	421	
1.898	8	412, 263	1.91
1.811	12	432	1.80 (broad)
1.780	7	254, 083	
1.716	6	225	
1.580	9	274, 462	1.57

* Calculated from the single-crystal X-ray diffraction data used for the structure determination on the co-type crystal no. G201b-LT2 (Rossi et al., 1986).

** Interplanar spacings measured from the Gandolfi photograph of Fig. 2.

etite and (2) that the breakdown of jadeite into albite + magnesio-alumino-taramite releases Na^+ and perhaps also Ca^{2+} and consumes H^+, then a largely balanced reaction can be written to relate lisetite growth with jadeite breakdown in different domains in the rock. A key feature of this reaction, and also of several alternative ones involving the breakdown of zoisite, is their constant Al/Si ratio (the Al/O ratio is almost constant also), which implies a considerable degree of Al-Si-O *immobility*.

Third, the fact that the calculated density of lisetite (D = 2.73) exceeds 2.66—the mean density of anorthite (D = 2.76) and of the pure Na equivalent of nepheline (D = 2.56)—suggests that lisetite is the higher P and/or lower T (i.e., higher P/T ratio) equivalent of such a combination of feldspar and feldspathoid. Likewise the combination of 1 lisetite + 4 quartz is more dense than its isochemical counterpart pure andesine ($An_{33.33}$), which implies that lisetite can be stable at higher P/T values than plagioclase. On the other hand the fact that all the Al is in the form of Al^{IV} strongly suggests that lisetite is not an eclogite-facies mineral since this facies is characterized by minerals with much greater Al^{VI} than Al^{IV}, except for specific cases where crystal-chemical constraints permit the survival of Al^{IV} at very high P, e.g., K-feldspar (Smith, 1982; Rossi, 1987). Thus on both a crystal-chemical and petrologic basis, the stability field of lisetite may be situated *between* the high P/T eclogite facies and the adjacent lower P/T metamorphic facies, i.e., in the uppermost (in the P direction) greenschist-, amphibolite-, or granulite-facies. This field may be estimated to lie just below and just above the reaction curve albite = jadeite + quartz, i.e., approximately in the range 10 ± 4 kbar at 400°C to 20 ± 4 kbar at 800°C.

Fourth, lisetite is now firmly established as a possible mineral structure in the well-known chemical system Ca-Na-Al-Si-O. However, this system is commonly represented in natural rocks by feldspars and feldspathoids at low P/T conditions (i.e., in igneous rocks) or by jadeite or grossular components in pyroxene and garnet solid solutions at high P/T conditions (i.e., in blueschists, eclogites, and kimberlite nodules). The *rarity* of lisetite may thus be attributed to a combination of the following three factors.

1. Metamorphism under P-T conditions in the *highest P part* of the amphibolite facies, which are not normally attained during classical regional prograde metamorphism. Such conditions can be expected to be achieved in a prograde manner by the prolonged subduction of relatively cool blueschist-facies terranes. At Liset, such conditions were arrived at by decreasing P from previous eclogite-facies conditions.

2. The Na- and Al-rich and K- and Mg-poor *extreme bulk-rock chemistry* provided by the Liset eclogite pod, whereby the K deficiency prevented the development of ordinary K-bearing nepheline and the Mg deficiency, relative to many other eclogites, led to a smaller proportion of Ca-Mg minerals and hence effectively left an excess of Ca.

3. A *very limited local diffusion of Al and Si,* which prevented nearby quartz from perturbing the locally high Al/Si ratio in the lathlike lisetite-bearing domains. The formation of coronitic rather than penetrative reaction zones is characteristic of most retrograde reactions in the Liset eclogite pod and implies static rather than dynamic conditions of retrograde metamorphism.

It is of course possible that lisetite is in fact more common in nature but has been overlooked because its optical properties are so similar to those of feldspars. Na-rich, K-poor subsilicic igneous rocks rich in nepheline and calcic plagioclase (e.g., theralite, nepheline-tephrite, or nepheline-basanite) might generate lisetite by prograde metamorphism if subducted to 10–20-kbar conditions. Otherwise the most probable environment for lisetite growth would be in K- and Mg-poor jadeite-, paragonite-, and zoisite-rich blueschists or eclogites retrograded by decreasing the P/T ratio without concomitant deformation that could promote Al-Si-O diffusion. The Liset eclogite pod is evidently the type example of such a scenario.

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