Naturally Occurring Crystalline Phases: Analogues for Radioactive Waste Forms

**Richard F. Haaker
Rodney C. Ewing**

January 1981

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ANALOGUES FOR RADIOACTIVE WASTE FORMS

Richard F. Haaker
Rodney C. Ewing
Department of Geology
University of New Mexico
Albuquerque, New Mexico 87131

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Pacific Northwest Laboratory
Richland, Washington 99352

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SUMMARY

Naturally occurring mineral analogues to crystalline phases that are constituents of crystalline radioactive waste forms provide a basis for comparison by which the long term stability of these phases may be estimated. The crystal structures and the crystal chemistry of the following natural analogues are presented:

- baddeleyite
- hematite
- nepheline
- pollucite
- scheelite
- sodalite
- spinel
- apatite
- monazite
- uraninite
- hollandite-priderite
- perovskite
- zirconolite

For each phase its geochemistry, occurrence, alteration and radiation effects are described. A selected bibliography for each phase is included.

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INTRODUCTION

Crystalline phase assemblages, such as supercalcine and SYNROC, have received increased consideration as possible alternatives to the borosilicate glass as a radioactive waste form. One criteria in selecting a waste form is the evaluation of its long-term "geologic" stability. The waste form is considered unstable should changes occur which cause phase degradation or increased radionuclide mobility. For crystalline phases these transformations may include: (1) physical degradation by mechanical forces, (2) alteration by leaching and diffusion mechanisms, (3) radiation damage in which the crystalline phases are converted to the metamict state, and (4) recrystallization in which new phases are formed by reaction between the waste form and the enclosing geologic medium.

Each of the above processes for waste forms may be modeled by the behavior of their naturally occurring analogues in different geologic environments. The objective of this report is to summarize the behavior of thirteen naturally occurring phases (Table 1) which serve as analogues to crystalline phases that appear in SYNROC and Supercalcine. This information may be used to estimate the long-term stability of crystalline waste forms and to verify the extrapolation of necessarily time-limited laboratory experiments.

For each of the naturally occurring analogues, their structure, chemistry, occurrence, age distribution, alteration effects and radiation damage effects are described. The reference section for each phase is separated into these topics. In order to provide the reader with ready access to the literature, selected references, which are not cited in the report, have been included. These additional references are not marked by an asterisk in the left margin. Because the geologic terminology may be unfamiliar to some readers, a glossary is included.

It is not always possible to identify natural analogues which are structurally or chemically comparable to the crystalline phases in the SYNROC or supercalcine (e.g. monoclinic baddelyite vs. tetragonal ZrO_2). However, structural and chemical differences between the crystalline waste phase and its natural analogue have been clearly identified.

Table 1: A Comparison of Natural Analogues to SYNROC and Supercalcine Phases.

Mineral	Waste Phase	Natural Phase	Comments
Baddeleyite	Tetragonal (Zr,RE,U)O _{2+x}	Monoclinic ZrO ₂	Tetragonal ZrO ₂ has no direct natural ² analogue.
Hematite	(Fe,Cr) ₂ O ₃	Fe ₂ O ₃ and Cr ₂ O ₃	Fe ₂ O ₃ is a common mineral while Cr ₂ O ₃ is rare.
Nepheline	NaAlSiO ₄	NaAlSiO ₄	Common
Pollucite	(Cs,Rb,Na)AlSi ₂ O ₆	(Cs,Na)AlSi ₂ O ₆ ·H ₂ O	The major cesium ore mineral.
Scheelite	(Sr,Ba,Ca)MoO ₄	CaWO ₄ , CaMoO ₄	Scheelite (CaWO ₄) is a major W ore mineral. CaMoO ₄ is very rare. BaMoO ₄ and SrMoO ₄ have not been reported as minerals.
Sodalite	AE ₂ (NaAlSiO ₄) ₆ (MoO ₄) ₂	Na ₈ Al ₆ Si ₆ O ₂₄ Cl ₂	Sodalite is a rock forming mineral. Natural sodalites do not have significant amounts of MoO ₃ .
Spinel	(Fe,Ni)(Fe,Cr) ₂ O ₄	NiFe ₂ O ₄ Fe ₃ O ₄ FeCr ₂ O ₄	Fe ₃ O ₄ is very common. FeCr ₂ O ₄ is a major Cr ore mineral. NiFe ₂ O ₄ is rare.

Table 1: A Comparison of Natural Analogues to SYNROC and Supercalcine Phases (Continued).

Mineral	Waste Phase	Natural Phase	Comments
Apatite	$AE.RE_4(SiO_4)_3O$	$A_5(SiO_4,PO_4)_3(O,OH,F)$ (A = Ca+RE+Th)	Silicate apatites are much less common than phosphate ones.
Monazite	$(Ce,Th,U)PO_4$	$(Ce,RE,Th,U,Ca)PO_4$	Relatively common, intensely studied.
Uraninite	$(U,Ce,Zr...)O_{2+x}$	ThO_2 CeO_2 UO_{2+x}	UO_2 is the major uranium mineral. ThO_2 is much less common while CeO_2 is very rare.
*Priderite	$Ba,Cs)_{2-x}Al_2Ti_6O_{16}$	$(K,Ba)_{2-x}(Fe,Al)_2Ti_6O_{16}$	Priderite is very uncommon and is not a close compositional analogue to SYNROC-"hollandite".
*Perovskite	$CaTiO_3$	$CaTiO_3$, also $(REE,Th,Ca,Na)_{1-x}TiO_3$	Rare earth rich perovskites are imperfect analogues for a waste phase near $CaTiO_3$. Not common but well characterized.
*Zirconolite	$CaZrTi_2O_7$	$(Ca,REE,Th,Zr)_2Ti_2O_7$	An uncommon mineral that may be quite durable.

* SYNROC phases

Although these data on natural analogues can never be used explicitly, they do allow the definition of boundary conditions under which particular structures and compositions may be stable. The natural analogues represent a long-term experiment, and their long-term stability in different geologic environments can be used to validate short-term laboratory experiments. These data can serve as a guide to the design and verification of appropriate laboratory experiments. However, the use of natural analogues will always be subject to the following limitations.

1. Some waste phases either do not have natural analogues, or their natural analogues are so rare that they are little more than mineral oddities (Table 1).
2. Transmutation effects of beta emitting fission products on the long-term stability of crystalline phases cannot be determined directly by the examination of natural analogues.
3. The effects of radiation damage due to short-lived TRU elements is a factor which has not been completely investigated.
4. It should be noted that radiometric age dates establish little more than upper limits to the longevity of crystalline phases. That a given mineral survives for periods in excess of 10^9 years under certain conditions, is not definite evidence for its survival under repository conditions.
5. Hydrothermal stability data for natural analogues are seldom available.
6. Kinetic data for waste and wall-rock interactions are essentially nonexistent. Without this data, one cannot predict whether the thermodynamic instability of waste form and wall-rock assemblages will be of any significance.
7. Finally, the reader should be reminded that descriptive mineralogy and geology often involve a large element of interpretation and that there may be errors in both fact and interpretation. In compiling this report, we have used the literature selectively in order to abstract that material which seems most pertinent to the issues raised in the selection of radioactive waste forms.

Most of the above limitations are due to a lack of hydrothermal, thermodynamic, kinetic and radiation damage data. The effects of radiation damage and transmutation are being determined experimentally and will provide information on optimal radioactive waste element concentrations. Hydrothermal, kinetic and thermodynamic data for crystalline phases are composition dependent and are best studied for simulated radioactive waste forms.

BADDELEYITE: ZrO_2

Baddeleyite (monoclinic ZrO_2) is an analogue for supercalcine zirconia (tetragonal $(\text{Zr}, \text{RE}, \text{U})\text{O}_2$). Baddeleyite is resistant to radiation damage and alteration. It occurs in a wide variety of rocks.

MINERAL DATA

Mineral data for baddeleyite are as follows:

Formula: ZrO_2

Crystal System:

Monoclinic

Space Group:

$P2_1/c$

Z:

4

Lattice Constants:

$a = 5.145 - 5.21 \text{ \AA}$

$b = 5.21 - 5.26 \text{ \AA}$

$c = 5.31 - 5.375 \text{ \AA}$

$\beta = 99^\circ 15'$

Mohs Hardness:

6 1/2

Density (gm/cm^3):

5.5 - 6.0 (meas)

5.825 (calc)

STRUCTURE

Three polymorphs of ZrO_2 are well established: cubic, tetragonal and monoclinic. Cubic ZrO_2 , the high temperature polymorph, has the fluorite structure (McCullough and Trueblood, 1959; Teufer 1962).

Tetragonal ZrO_2 is stable at intermediate temperatures. Its structure may be regarded as a tetragonal distortion of the cubic fluorite structure. Teufer (1962) reports the following crystal data for tetragonal ZrO_2 :

Space group: $P4_2/nmc$
 $a = 3.64 \text{ \AA}$, $c = 5.27 \text{ \AA}$ (at 1250°C)
 $Z = 2$

The corresponding pseudo-cubic unit cell for tetragonal ZrO_2 is:

Space group: $C4_2/acm$
 $a = 5.15 \text{ \AA}$
 $c = 5.27 \text{ \AA}$
 $Z = 4$

Baddeleyite, apparently the only naturally occurring ZrO_2 polymorph, has a grossly distorted fluorite structure. Smith and Newkirk (1965) report the following crystallographic data for synthetic baddeleyite:

Space group: $P2_1/c$
 $a = 5.145(5) \text{ \AA}$, $b = 5.2075(5) \text{ \AA}$
 $c = 5.3107(5) \text{ \AA}$, $\beta = 99^\circ 14(5)'$
 $Z = 4$

In the baddeleyite structure a slightly distorted square array of oxygen ions alternate with distorted layers of oxygen ions parallel to (100). One half of the interstitial voids are occupied by Zr^{+4} ions. Zr ions coordinate to seven (not eight) oxygen ions.

The monoclinic to tetragonal phase transformation requires a change in coordination number and a considerable volume change (about 6 percent (Grain and Garvie, 1965)). According to Baun (1963), the monoclinic phase begins to transform at 1000°C and the last monoclinic phase disappears at 1180°C . The reverse transforma-

tion begins to occur at 970°C and the last tetragonal phase disappears at 750°C . The tetragonal to cubic transformation is displacive, occurring at $2285 \pm 50^{\circ}$ with a 15° hysteresis (Smith and Cline, 1962).

CHEMISTRY

Baddeleyite usually contains 1 - 2 weight percent Hf, and may contain REE, Ca, Th, U and impurities such as Fe, Si, Mg, Mn and Ti in amounts of 0.1 - 3 weight percent, Table 2.

The system ZrO_2 - ThO_2 has been studied by Duwez and Loh (1957) and Mumpton and Roy (1959). Only minor amounts of UO_2 or ThO_2 dissolve in the baddeleyite structure, especially at temperatures below 1000°C at which these minerals have formed (Mumpton and Roy, 1959). Below 400°C , under hydrothermal conditions (1-4 Kbar) a continuous series of solid solutions with the fluorite structure occur with compositions varying from ThO_2 to almost pure ZrO_2 , Figure 1. X-ray diffraction patterns of the cubic solid solutions indicate this phase is poorly crystalline. This cubic solid solution phase exsolves when reheated at higher temperatures. About 8 mole percent ZrO_2 dissolves in UO_2 and less than 4 mole percent UO_2 in ZrO_2 at temperatures up to 1300°C (Mumpton and Roy, 1959). The monoclinic-tetragonal transition temperature of ZrO_2 in the system ZrO_2 - ThO_2 is 1000°C . Solid solution of ZrO_2 in ThO_2 and vice versa is only about 2 percent at this temperature (Mumpton and Roy, 1959).

Ono (1972) reports the phase transformation of $(\text{Zr}, \text{Ce})\text{O}_2$ from monoclinic to tetragonal is martensitic and depends on the transformation cycle, grain size, impurity contents and thermal history. It is characterized by heterogeneous nucleation and a wide temperature range for coexisting polymorphs. The transition temperatures, Table 3, indicate that the addition of small amounts of CeO_2 to ZrO_2 causes drastic changes in transition temperatures. ZrO_2 - Y_2O_3 and ZrO_2 - CaO solid solutions also show significant depression in phase transition temperatures. Y_2O_3 or CaO stabilized tetragonal zirconia is

Table 2: Chemical Analyses of Baddeleyite, Monoclinic ZrO_2 , in weight percent (Vlasov, 1966).

Components	Balangoda, Ceylon	Jacupiranga, Brazil	Minas Gerais, Brazil	Balangoda, Ceylon	Palabora, South Africa
$(\text{Na}, \text{K})_2\text{O}$	--	0.42	--	--	--
CaO	0.6	0.55	--	0.24	0.80
MgO	--	0.1	--	--	0.64
MnO	--	--	trace	0.04	0.23
Al_2O_3	--	0.43	0.40	0.07	--
$(\text{Y}, \text{Ce})_2\text{O}_3$	--	--	--	0.04	--
Fe_2O_3	0.82	0.41	0.92	0.34	2.10
SiO_2	0.19	0.70	0.48	0.45	0.06
TiO_2	--	--	0.48	0.13	1.65
ZrO_2	98.90	96.52	97.19	97.22	95.20
H_2O	--	--	0.38	--	--
Loss on ignition	0.28	0.39	--	0.67	undetected
Total	100.25	99.52	99.85	99.20	100.68
Specific gravity	5.72	--	5.538	--	6.025

Figure 1: Phase diagram for the system ZrO_2 - ThO_2 at subsolidus temperatures. Part of the data above 1000 $^{\circ}\text{C}$ are from Duwez and Loh (1957), Mumpton and Roy (1959).

Table 3: Monoclinic-Tetragonal Transition Temperatures for (Zr, Ce)O₂ (Ono, 1972).

CeO ₂ Content Mole Percent	Annealing Temperature °C	Sintered (S) or Powder (P)	Duration (Hours)	Transition Temperature	
				On Heating	On Cooling
8	1600	S	18	602 ± 10°C	540 ± 10°C
8	1250	S	96	613	505
8	1250	P	25	620	490
9	1400	S	14	530	480
9 ^a	1320	P	14	530	470
9 ^a	1320	P	24	515	
10 ^b	1400	P	7.5	445	364
10 ^b	1330	P	12	445	353
10 ^b	1400	S	45	405	

a. Very small amount of tetragonal phase is observed at room temperature.

b. About 10 percent of tetragonal phase is observed at room temperature.

not known to occur in nature, but is of some importance as a refractory ceramic formulation.

The $\text{ZrO}_2 - \text{HfO}_2$ system has been studied by Ruff and Ebert (1929), Cohn and Tolksdorf (1930), Geller and Yavorsky (1945), Dietzel and Tober (1953), Curtis *et al.*, (1954) and Mumpton and Roy (1959). Mumpton and Roy showed that the HfO_2 content of zirconia effects the temperature at which the monoclinic tetragonal transformation begins. The transformation begins about 20°C higher in "natural" ZrO_2 , containing 2 weight percent more Hf than in pure ZrO_2 .

Ono (1972) studied the system $\text{ZrO}_2 - \text{TiO}_2$ and developed a phase diagram, Figure 2. At 1300°C and 1650°C , the limits of solubility of TiO_2 in ZrO_2 are 14 ± 1 and 20 mole percent respectively. ZrO_2 solid solutions containing greater than 5 percent TiO_2 are metastable below 1080°C (Ono, 1972).

A phase diagram for the system $\text{ZrO}_2 - \text{SiO}_2$ has been proposed by Buttermann and Foster (1967), Figure 3. Approximately 33 weight percent SiO_2 is taken into ZrO_2 at temperatures below 1600°C . Zircon (ZrSiO_4) is the only zirconium silicate in the system. In the presence of free silica (quartz), Zircon (ZrSiO_4) should be favored over baddeleyite (ZrO_2).

OCCURRENCE

Zircon (ZrSiO_4) and baddeleyite are the major zirconium minerals. Baddeleyite occurs in carbonatites, kimberlites, hydrothermally altered nepheline syenites and tinguaite, gabbros, lunar basalts, granitic pegmatites, tektites and in placer deposits.

In carbonatites, baddeleyite is a high temperature mineral associated with pyrochlore ($\text{Ca}_2\text{Nb}_2\text{O}_7$) and apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH},\text{F})$), and is formed during the initial stages of carbonatite formation (Vlasov, 1964). Colloform and fibrous baddeleyite in the nepheline syenites are associated with secondary minerals such as zeolites and clay minerals. In the gabbros of Axel Heiberg Island, Canadian

Figure 2: ZrO₂ - TiO₂ phase diagram. T = tetragonal, M = monoclinic, ZT = ZrTiO₄, R = rutile, x = inversion temperature on cooling, . = inversion temperature on heating (Ono, 1972).

Figure 3: Phase diagram for the system ZrO_2 - SiO_2 (Butterman and Foster, 1967).

Arctic Archipelago, it occurs interstitially and embedded in augite (a pyroxene mineral), and is frequently associated with apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH},\text{F})$) (Keil and Fricker, 1974). In lunar basalts it also occurs interstitially and is commonly associated with silica, silica rich glass, K-feldspar (KAlSi_3O_8), apatite and whitlockite ($\text{Ca}_3(\text{PO}_4)_2$) (Keil, Prinz and Bunch, 1971; El Gorsey et al., 1972; Lovering et al., 1972; Dowty et al., 1973). In tektites and impact glasses, it is formed from zircon (ZrSiO_4) as a result of the high temperature volatilization of silica:

(El Gorsey, 1965; Clarke and Wosinski, 1967; Kleinman, 1969). Baddeleyite (ZrO_2) may also be formed by heating metamict zircon (Ueda, 1957; Lima de Faria, 1964). Akhmanova and Leonova (1961) observed no phase separation.

A rare occurrence of baddeleyite (ZrO_2) from cavities of sanidine lavas in Italy is associated with fluorite (CaF_2), nepheline ($\text{NaAlSi}_3\text{O}_8$), pyrochlore ($\text{Ca}_2\text{Nb}_2\text{O}_7$) and allanite ($(\text{Ca},\text{RE},\text{Th})_2(\text{Al},\text{Fe},\text{Mg})_3(\text{SiO}_4)_3\text{OH}$) (Vlasov, 1964).

Baddeleyite occurs in the United States in a corundum syenite near Bozeman, Montana and in tektites from Martha's Vineyard and Georgia. It also occurs as rolled pebbles in Brazil, in Sweden, in Italy, on Axel Heiberg Island (Canadian Arctic Archipelego); in carbonatite rocks in Eastern Transvaal, as detrital material in placers in Zaire and Ceylon, and in the impact glasses of the Ries and Aouelloul Craters.

ALTERATION

Baddeleyite is an extremely durable mineral and references to alteration and weathering of it are rare in the geologic literature. It is sufficiently durable to occur as baddeleyite sand along with resistant minerals such as garnet ($(\text{Ca},\text{Mg})\text{Al}_2\text{Si}_2\text{O}_{12}$), zircon (ZrSiO_4), rutile (TiO_2) and thorite (ThSiO_4) (Gottardi, 1952).

Because of its high degree of thermal stability and its resistance to corrosion, baddeleyite (ZrO_2) is a widely used ceramic material. Stabilized tetragonal zirconia may or may not have the durability of baddeleyite, but since it is not a natural phase this cannot be inferred from the geologic literature. Several studies of corrosion and engineering properties of stabilized zirconia refractories are listed in the reference section.

Zirconium contents of mineral waters and subsurface waters of central Asia have been measured by Chernikov and Korsakov (1966). They observed Zr concentrations of up to .2 ppm. In a study of the mobility of trace elements, it was found that Zr migrates more slowly than Be, La, Sn, Sc, Y and Ga (Mistevich, 1961). Solubility studies by Popa and Arsenie (1969) indicate that ZrO_2 is practically insoluble in HCl , HNO_3 , their mixtures and in concentrated base. Slight solubility is observed in 65 percent H_2SO_4 and in concentrated KHSO_4 and NaHSO_4 .

RADIATION EFFECTS

The effects of neutron irradiation on ZrO_2 which was stabilized by 6 percent Y_2O_3 have been studied at 650° , 875° and 1025° (Clinard, Rohr and Rankin, 1977). The largest amount of volume increase ($\Delta v/v$) was 1.76 percent. The volume change at 875° was accompanied by a high concentration of dislocation loops. At the highest fluences, pore-like defects were observed by TEM. It was speculated that these defects may be aggregates of metal colloids, oxygen filled inclusions or voids (Clinard, Rohr and Rankin, 1977). Only rarely, if ever, does baddeleyite (ZrO_2) occur in the metamict state (Ueda, 1957).

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HEMATITE GROUP: Fe_2O_3 , Cr_2O_3

Hematite (Fe_2O_3) and eskolaite (Cr_2O_3) are analogues for the supercalcine corundum structure phase, $(\text{Fe,Cr})_2\text{O}_3$. Fe_2O_3 and Cr_2O_3 are stable under surface conditions. Fe_2O_3 occurs in igneous rocks, metamorphic rocks, sediments and soils.

MINERAL DATA

Mineral data for hematite group minerals are as follows:

Formula:	Hematite (Fe_2O_3)	Eskolaite (Cr_2O_3)
Crystal System:	Trigonal	Trigonal
Space Group:	$\bar{R}3c$	$\bar{R}3c$
Z:	6 (hexagonal)	6 (hexagonal)
Lattice Constants:	(hexagonal) a = 5.0317 Å c = 13.737 Å	(hexagonal) a = 4.958 - 4.973 Å c = 13.57 - 13.60 Å
Mohs Hardness:	5 - 6	(?)
Density (gm/cm^3):	5.26 (Meas.) 5.256 (Calc.)	5.18 - 5.215

STRUCTURE

Hematite (Fe_2O_3) and eskolaite (Cr_2O_3) have the corundum structure. The structure has $R\bar{3}c$ space group symmetry and consists of alternating layers of oxygen and iron perpendicular to the threefold axis (Pauling and Hendricks, 1925). The oxygens are in a slightly distorted hexagonal close packed arrangement. Successive cation layers contain equal numbers of ions in sixfold coordination. Two thirds of the octahedral sites are occupied. This differs from the spinel structure (cubic AB_2O_4) where two thirds of the cations in alternate layers are in four-fold coordination (Lindsley, 1976).

The distorted FeO_6 octahedra occupy layers stacked six high normal to the c-axis (Blake *et al.*, 1966). In each octahedron one half of the edges which are not in the basal plane are shared; the other half are unshared. In addition, each octahedron has one shared and one unshared face parallel to the basal plane.

Hematite is antiferromagnetic (Neel, 1949) with alternate planes of Fe^{+3} along (0001) magnetized in opposite directions, so that the net magnetic moment is zero. A review of the magnetic properties of hematite is given by Dunlop (1971).

CHEMISTRY

Natural hematite is composed predominately of Fe_2O_3 although small amounts (one percent) of MnO , FeO and TiO_2 may be present, Table 4. Appreciable amounts of SiO_2 and Al_2O_3 may represent contamination, while large amounts of TiO_2 may be due to ilmenite intergrowths (Deer *et al.*, 1966). Ta, Ti, In, Ni, Mo, V, Zn, Cr, Cu, and Be have been listed as accessory elements in magnetite (Petrunkov, 1966).

At 800°C , only 5 weight percent TiO_2 is soluble in the hematite structure (Basta, 1953), but at temperatures of more than 1050°C , hematite and ilmenite (FeTiO_3) form complete solid solutions (Nicholls, 1955). At high temperatures, the structures of the two minerals are

Table 4: Chemical Analyses of Hematite (Deer et al., 1962).

	1.	2.	3.	4.
Fe_2O_3	99.52	98.14	98.00	96.86
FeO	-	1.29	1.39	-
Mn_2O_3	-	0.54	-	-
MnO	-	0.38	-	0.19
MgO	-	-	0.02	-
Al_2O_3	-	-	-	1.26
TiO_2	0.10	-	0.34	-
SiO_2	-	-	0.24	0.41
H_2O^+	-	-	-	1.73
Total	99.62	100.35	99.99	100.45
Density (gm/cm^3)	5.31	-	5.31	4.48

equivalent. The unit cell volume of hematite increases with increasing mole percent ilmenite (Lindsley, 1965). Ishikawa (1958b), Shirane et al. (1962) and Hoffman (1975) have studied the magnetic properties of the hematite-ilmenite series.

The hematite-ilmenite solid solution is found in all metamorphic grades in many rock types, Table 5 (Rumble, 1976). Since there is limited miscibility at metamorphic temperatures along the Fe_2O_3 - FeTiO_3 join, exsolution lamellae of ilmenite in a hematite host or vice versa are common, Figure 4 (Lindsley, 1976).

Hematite-ilmenite exsolution is found in deep-seated intrusions, particularly in anorthosite and other basic suites, but is also present in granitic suites (Haggarty, 1976). Exsolution mechanisms are discussed by Kretchsmar and McNutt (1971).

Small amounts (one percent) of magnetite (Fe_3O_4) can be taken into solid solution at 1452°C with $f(\text{O}_2) = 1$ atm (Greig et al., 1935). Only at very high temperatures is there considerable stable solid solution (Lindsley, 1976). The composition of magnetite in equilibrium with hematite and corundum was determined by Turnock and Eugster (1962). Approximately 10 weight percent Al_2O_3 goes into solid solution with hematite at 1300°C (Muan and Gee, 1955).

Eskolaite (Cr_2O_3) is a rare mineral in comparison with hematite and chromite (FeCr_2O_4). Although a complete solid solution series exists between Fe_2O_3 and Cr_2O_3 (Katsura and Muan, 1964), both minerals tend to occur as end-members. Hematite (Fe_2O_3) usually contains only traces of Cr, Table 4, while eskolaite (Cr_2O_3) contains up to a few weight percent Fe (Kouvo and Vuorelainen, 1958). The Fe_2O_3 - Cr_2O_3 - FeO phase diagram is discussed in the spinel section of this report.

Eskolaite formation in chrome spinel has been observed during heating experiments (Kouvo and Vuorelainen, 1958). It has also been observed to be a product of the thermal decomposition of uvarovite, a garnet of composition $\text{Ca}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$ (Huckenholz and Knittel, 1976).

Table 5: Hematite Containing Oxide Mineral Assemblages in Metamorphic Rocks (Modified from Rumble, 1976).

	Oxide Mineral Assemblage					High-Pressure Metamorphism
	Chlorite and Biotite	Garnet and Staurolite	Sillimanite	Sillimanite-potash Feldspar	High Temperature contact metamorphism	Sanbagawa terrane glaucophane and epidote-amphibolite
	Rutile-hematite	*	*	*	*	*
	Hematite	*	*	*		*
29	Hematite-ilmenite	*	*	*		*
	Magnetite-hematite	*	*	*		*
	Ilmenite-hematite-magnetite	*	*	*		*
	Pleonaste-hematite-magnetite			*	*	*
	Pseudobrookite-hematite-magnetite				*

Figure 4: The Fe_2O_3 - FeTiO_3 phase diagram (Carmichael, 1961) (Curve). Stipples represent miscibility gap area reported by Lindsley (1973) based on homogenization experiments. The actual location of the miscibility gap within the stippled area has not been determined. P means pseudo-brookite (Psbss) was present in the runs, R means that rutile was present.

OCCURRENCE

Hematite (Fe_2O_3) occurs extensively in thick beds of sedimentary origin, as an accessory mineral in igneous rocks and as a sublimation product in lavas, in metamorphic rocks and in vein deposits. It is also found in soils as a weathering product of iron-bearing minerals.

In many sedimentary hematite ore deposits, solutions metasomatically introduce hematite in the rock, the iron frequently being derived from the weathering of overlying sediments. It is found as a cementing medium in sandstone and as oolitic hematite associated with limestone. Hematite causes much of the red coloration in rocks.

Hematite occurs in granites, syenites, rhyolites, trachytes and other igneous rocks poor in ferrous iron, and as a late-stage product of volcanic activity as crystals sublimated on earlier material. Specular hematite (i.e., hematite with a metallic luster) is found in highly kaolinized (i.e., partially weathered to clay) Dartmoore granite where bands of the ore are associated with sericite (a mica), quartz, tourmaline (a borosilicate mineral) and cassiterite (SnO_2) (Henson, 1957). Hematite (Fe_2O_3) is also found in sulfide skarns (Bogolepov, 1959). It is found associated with chlorite ($(\text{Mg}, \text{Al}, \text{Fe})_{12}(\text{Si}, \text{Al})_8\text{O}_{20}(\text{OH})_{16}$) as pseudomorphs after olivine ($(\text{Mg}, \text{Fe})_2\text{SiO}_4$) in basalt (Smith, 1959). It is often seen as exsolved material in iron oxide minerals such as ilmenite (FeTiO_3). Intergrowths of hematite (Fe_2O_3) and magnetite (Fe_3O_4) have been reported by Edwards (1949) and Baker (1955). It is also found as a supergene replacement (oxidation product) of magnetite (Fe_3O_4) (Ramdohr, 1969).

Hematite results from the metamorphism of magnetite (Fe_3O_4), siderite (FeCO_3) and hydrated iron oxides, and is found in a variety of metamorphic zones, Table 5. It is common in metamorphosed Precambrian banded iron ores in jasper (impure quartz) beds. Deposits up to 300 meters in thickness occur in numerous places in the United States and throughout the world.

Eskolaite occurs in Yugoslavia as a metamorphic product of

chromite (FeCr_2O_4). Hematite (Fe_2O_3), ilmenite (FeTiO_3) and ulvospinel (TiFe_2O_4) were present in the same samples (Grafenauer, 1960). It occurs in rounded pebbles in British Guiana as an aggregate with quartz, pyrophyllite ($\text{Al}_4\text{Si}_8\text{O}_{20}(\text{OH})_4$) and possibly other chromium oxides (Milton and Chao, 1958). In an occurrence in Finland, it is associated with an extensive list of minerals (Kouvo and Vuorelainen, 1958).

ALTERATION

Alteration products of hematite include magnetite (Fe_3O_4), goethite ($\text{FeO}(\text{OH})$), pyrite (FeS), and siderite (FeCO_3) (Deer et al., 1962).

Experimental work by MacChesney and Maun (1959) on the system iron oxide- TiO_2 has shown that hematite is the stable phase of pure iron oxide up to 1390°C when heated in air. At 1390°C hematite dissociates into magnetite (Fe_3O_4) plus O_2 , the stable phases up to the liquidus temperature of 1594°C . With the addition of 10 weight percent TiO_2 , the hematite-magnetite decomposition temperature rises from 1390°C to 1524°C .

Bedarida et al., (1973) studied the alteration of hematite to goethite (orthorhombic, $\text{FeO}(\text{OH})$). They suggested hematite weathers by the following sequence: Hematite $\longrightarrow$ aqueous surface solution of hematite $\longrightarrow$ goethite nucleation in water $\longrightarrow$ water evaporation and formation of a crystalline crust of goethite. The weathering starts along the steps of the (0001) faces, where randomly oriented acicular crystals form. The acicular crystals aggregate to form balls which in turn aggregate in an ordered linear growth pattern along crystallographic directions. The rows of balls merge to form a crust of goethite.

At temperatures below 675°C hematite may form pyrite and SO_2 gas in the presence of sulphur (Kullerud, 1957). In the system Fe-S-O the reaction pyrite + magnetite = pyrrhotite + hematite takes place at about 675°C . Between 675°C and 700°C , the stable

assemblages are pyrite-pyrrhotite-hematite and magnetite-pyrrhotite. Above 700°C neither hematite nor magnetite is stable with the pyrite-pyrrhotite assemblage. Above 743°C hematite, magnetite and pyrrhotite is the stable phase assemblage (Deer et al., 1962).

Rowland and Jones (1949) using DTA curves for siderite, showed that on heating to 700°C, hematite and a magnetite-like mineral were produced. At 800°C, a change probably representing the γ -Fe₂O₃ (maghemite, defect spinel structure) to α -Fe₂O₃ (hematite) transition was noted. Finch and Sinha (1957) have also studied the γ to α transition.

HEMATITE

Structure

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NEPHELINE GROUP: $(\text{Na,K})\text{AlSiO}_4$, KAlSiO_4

Nepheline, $(\text{Na,K})\text{AlSiO}_4$ is an analogue for the supercalcine nepheline phase, NaAlSiO_4 . Nepheline has a tridymite derivative structure. Nepheline is not stable with silica saturated (granitic rocks) at high temperatures.

MINERAL DATA

Mineral data for nepheline and kalsilite are as follows:

Formula:	Nepheline ((Na,K)AlSiO ₄)	Kalsilite (KAlSiO ₄)
Crystal System:	Hexagonal	Hexagonal
Space Group:	P6 ₃	P6 ₃
Z:	8	2
Unit Cell Parameters:	a = 9.94 - 10.09 c = 8.31 - 8.49 A	a = 5.15 - 5.2 c = 8.67 - 8.7 A
Mohs Hardness:	5.5 - 6	6
Density (gm/cm ³):	2.55 - 2.665 meas. 2.653 calc.	2.59 - 2.625 meas.

STRUCTURE

Nepheline and kalsilite are not isostructural, but both structures are based upon the tridymite framework in which one half of the silicon atoms are replaced by aluminum atoms. Charge neutrality is maintained by adding alkali ions to the voids.

Kalsilite (KAlSiO_4) has $P6_3$ space group symmetry: $Z = 2$, $a = 5.16$ A, $c = 8.69$ A, and $D = 2.62$. In kalsilite, Figure 5, potassium lies on the 6_3 axis and is coordinated with nine oxygen atoms. The average potassium-oxygen interatomic distance is 2.97 A. The occupancy of the tetrahedral sites by Al and Si atoms is ordered. In Figure 5, all of the tetrahedra which point toward the reader are occupied by aluminum atoms, those pointing away are occupied by silicon atoms. All of the tetrahedra are centered on threefold axes. Since oxygen atom O2 is displaced about .25A from the threefold axis it is disordered. The distribution of O2 among its three sites may not always be statistical, some natural kalsilites show evidence of having a superstructure (Perrotta and Smith, 1965). Earlier, Smith and Sahama (1957) suggested that the presence of superstructure reflections may be due to aluminum and silicon ordering characteristics of the tetrahedral sites.

Nepheline like kalsilite belongs to space group $P6_3$: $Z = 8$, $a = 10.01$ A, $c = 8.4$ A and $D = 2.59 - 2.625$ (cf. kalsilite). It has less symmetry per unit volume or per $(\text{alkali})\text{AlSiO}_4$ formula than kalsilite, Figures 5 and 6. The severe distortion of the tridymite framework results in voids of two types. The largest voids contain potassium ion which is coincident with a 6_3 axis. Each potassium ion is coordinated by nine framework oxygen atoms. The 6_3 axes in the kalsilite structure which are not present in the nepheline structure are reduced to 2_1 axes and are coincident with a second, smaller, void. Each of the smaller voids is occupied by sodium in a general position (Hahn and Buerger, 1955). The large and small voids occur in the ratio 2:6 (Deer, Howie and Zussman, 1963). Occupancy of the tetrahedral sites coincident with the threefold axes is ordered (cf.

Figure 5: Four unit cells of the kalsilite structure projected onto (001). A fifth unit cell showing positions of the symmetry elements of $P6_3$ is included as an aid in visualizing the structure (Perrotta and Smith, 1965).

Figure 6: The structure of nepheline projected onto (001). Only the lower half of the framework is included. The upper and lower halves of the framework are related by 6_3 and 2_1 axes (Hahn and Buerger, 1955).

kalsilite), while tetrahedral sites in general positions appear to have Al-Si disordering (Hahn and Buerger, 1955).

Variation of unit cell parameters and bond distances for nepheline as a function of temperature have been investigated by Foreman and Peacor (1970). The unit cell volume of nepheline shrinks by about four percent when cooled from 1000°C to 100°C.

CHEMISTRY

In addition to structural differences among members of the nepheline-kalsilite system, polymorphism is present over much of the series and complicated by Si-Al ordering on tetrahedral sites (Dollase, 1970) and cation ordering in inter-framework voids (Samsonova, 1970). All the phases in the nepheline-kalsilite system have been identified, Table 6 and a phase diagram for this system has been proposed, Figure 7. Above 800°C the phase diagram becomes complicated. Four polymorphs of NaAlSiO_4 are known. High-carnegieite (cubic) is stable from the liquidus down to 1250°C, where it transforms to high-nepheline (orthorhombic). At 900°C high-nepheline inverts to low-nepheline (hexagonal) which is stable to room temperature. The transformation of high-carnegieite to high-nepheline is sluggish. By quenching, high-carnegieite can be obtained in the nepheline stability field, but at 690°C it undergoes a displacive inversion to low-carnegieite.

Five polymorphs of KAlSiO_4 are known. Below 850°C, kalsilite (hexagonal) is stable. Near 1000°C, synthetic kaliophilite (hexagonal) has been obtained but the remainder of the laboratory syntheses from 900°C to the liquidus have yielded orthorhombic KAlSiO_4 . The synthetic kaliophilite is not identical to natural kaliophilite, but their powder patterns are similar. Anomalous natural kaliophilite is also known.

Below 1100°C a solvus exists between kalsilite of composition Ne_0 and low-nepheline of composition Ne_{71} . Above the solvus kalsilite has been obtained from Ne_0 to Ne_{20} and nepheline is the stable phase

Table 6: Principal Properties of the phases in the Nepheline- Kalsilite System (Smith and Tuttle, 1957).

Name	Range of Composition, Wt. percent NaAlSiO_4	Symmetry	a	b	c
nepheline	30 - 100	hexagonal	10.0	---	8.4
high-nepheline	near 100	orthorh.	10.2	17.6	8.5
kalsilite	0 - 20	hexagonal	5.2	---	8.7
orthorhombic KAlSiO_4	0 - 10	orthorh.	9.1	15.7	8.6
high-carnegieite	90 - 100	cubic	7.3	---	---
low-carnegieite	90 - 100	low-symm.	?	?	?
tetrakalsilite	near 30	hexagonal	20.5	---	8.5
"0 2"	near 20	orthorh.	8.9	10.5	8.5
natural kaliophilite	0 - 10	hexagonal	26.9	---	8.5
anomalous natural kaliophilite	0 - 10	hexagonal	26.9	---	8.5
synthetic kaliophilite	0 - 10	hexagonal	5.2	---	8.6

Figure 7: A phase diagram for the system NaAlSiO_4 - KAlSiO_4 . The dashed lines are inferred phase boundaries. Cg = carnegieite, L = liquid, Ne_h = high temperature nepheline, Ne = low temperature nepheline, O_1 = orthorhombic KAlSiO_4 , Ks = kalsilite, and H_4 = tetrakalsilite (Tuttle and Smith, 1958).

above the solvus for compositions containing more soda than Ne_{30} . Both nepheline and kalsilite solid solutions may be quenched to room temperature without unmixing. Two phases, tetrakalsilite (hexagonal) and orthorhombic tetrakalsilite, have been obtained in the composition range Ne_{20-30} .

Phase equilibrium relations in the system $\text{NaAlSiO}_4 - \text{NaAlSi}_3\text{O}_8 - \text{H}_2\text{O}$, both stable and unstable, have been investigated, Figure 8, (Saha, 1961). The known mineral phases in this system are nepheline (NaAlSiO_4), albite ($\text{NaAlSi}_3\text{O}_8$), jadeite ($\text{NaAlSi}_3\text{O}_8$), analcite ($\text{NaAlSi}_2\text{O}_6$, a zeolite) and natrolite ($\text{Na}_3\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$). Nepheline hydrate I ($\text{NaAlSiO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$), nepheline hydrate II ($\text{NaAlSiO}_4 \cdot 1/4\text{H}_2\text{O}$), zeolite "A" ($\text{NaAlSiO}_4 \cdot 2.35\text{H}_2\text{O}$) and zeolite "B" are other phases in the system: Nepheline-Na-feldspar- H_2O .

Nepheline (NaAlSiO_4) is relatively insoluble in albite ($\text{NaAlSi}_3\text{O}_8$), but takes up to 33 percent by weight albite in solid solution at 600°C and 1 kbar. (Saha, 1961; Greig and Barth, 1938). The eutectic temperature is $1068^\circ \pm 5^\circ\text{C}$ at a composition of $\text{Ab}_{76}\text{Ne}_{24}$. MacKenzie (1954) found the minimum melting temperature to be $870^\circ \pm 5^\circ\text{C}$ at the composition $\text{Ab}_{72}\text{Ne}_{28}$. He also found the limit of solid solution to be 25 percent by weight albite in nepheline at 740°C .

OCCURRENCE

Nepheline is the characteristic mineral of the alkaline rocks and is the most common feldspathoid (Deer et al., 1963). Nepheline is associated with alkali feldspars in the nepheline syenites and gneisses, and with plagioclase ($(\text{Na,Ca})\text{Al}(\text{Al,Si})\text{Si}_2\text{O}_8$) in rocks of the gabbro clan. In the basic alkaline and ultra-alkaline rocks, nepheline occurs with the common ferromagnesian minerals and sodium pyroxenes and amphiboles ($((\text{Mg,Fe,Ca})_2(\text{Mg,Fe,Al})_5(\text{Si,Al})_3\text{O}_{22}(\text{OH}))$), but not with orthopyroxene ($(\text{Mg,Fe})\text{SiO}_3$) or pigeonite ($(\text{Mg,Fe,Ca})-(\text{Mg,Fe})\text{Si}_2\text{O}_6$). It occurs with melilite ($((\text{Ca,Na})_2(\text{Mg,Fe,Al,Si})_3\text{O}_7$), monticellite (CaMgSiO_4) and wollastonite (CaSiO_3) in some calcium basic rocks, and with leucite (KAlSi_2O_6) in some potassium hypa-

Figure 8: Isobaric (1 kbar), isothermal sections for the system $\text{NaAlSiO}_4 - \text{NaAlSi}_3\text{O}_8 - \text{H}_2\text{O}$. Data plotted in mol. percent. $\text{NaAlSi}_3\text{O}_8$, NaAlSiO_4 and H_2O constitute the three components; it is assumed that the system is ternary (Saha, 1961).

byssal and volcanic rocks. Nepheline and quartz (hence granites) cannot stably coexist. The three common nepheline parageneses are as a primary phase of magmatic crystallization, as a product of metasomatism (nephelinization), and as a result of reaction (contamination) of both acid (high silica) and basic (low silica) magmas with calcium sediments. Plutonic nephelines are ordered and volcanic nephelines are disordered (Sahama, 1962).

The compositions of nephelines from nepheline syenites and nepheline gneisses range approximately between $\text{Ne}_{73}\text{Ks}_{27}$ and $\text{Ne}_{75}\text{Ks}_{21}\text{Q}_4$. In these rocks nepheline is associated with low temperature feldspars. In volcanic rocks, nepheline compositions vary widely in response to different host rock compositions. In volcanic rocks the associated feldspars are of the high temperature series. The contrast between plutonic and volcanic nephelines is related to structure. Nephelines approaching the ideal composition $\text{Na}_3\text{KAl}_4\text{Si}_4\text{O}_{16}$ are characteristically associated with lower temperatures of crystallization; at higher temperatures the tolerance of both alkali sites for greater departures from the ideal composition is increased.

Many nepheline rocks are metasomatically formed and are derived from a variety of earlier rocks, including limestones and amphibolites. Nephelinization is used to describe a series of related processes which result in the formation of nepheline rocks, the varied mineralogy of which is dependent on the composition of both pre-existing rocks and the fluids involved.

Local occurrences of nepheline rocks may form by the reaction of basic magmas with carbonate sediments. They may also develop by limestone contamination of intermediate composition magmas. Limestone assimilation in magmas was considered by petrologists to be the primary cause of the formation of nepheline rocks. This process has subsequently been shown to be untenable in many instances, and is no longer generally accepted.

Kalsilite and Kaliophilite are very rare minerals. They are restricted to volcanic rocks exceptionally poor in sodium.

Since nephelines contain between 3 and 10.2 percent K_2O , their

potential K/Ar dating has been investigated (McIntyre, et al., 1966; Shafiqullah, et al., 1969). High retention of argon has been noted. K/Ar ages of nepheline compared with those of coexisting biotites and amphiboles are older. Ages for some nephelines are given in Table 7.

ALTERATION

Experimental investigations suggest that nepheline is not stable below 400 - 500°C at moderate to high pressure in the presence of excess water. Glasses of nepheline composition, heated to 265 - 450°C at various pressures, crystallize directly nepheline hydrate 1 and some paragonite (Saha, 1961). Nepheline crystals are directly converted to analcite when heated in the interval 300 - 395°C and 2 - 3 kbar.

Many authors have reported alteration products of nepheline from natural and synthetic reactions, Table 8. Alteration rinds and complete replacements of nepheline have often been called "hydronepheline". Barrer and White (1952) have suggested that the "hydronepheline" may be nepheline hydrate 1, but no x-ray data are available. Tilley and Harwood (1931) report that their "hydronepheline" is uniaxial positive with $n_w = 1.490$ and $n_e = 1.500$. These optical properties are in close agreement with those of nepheline hydrate 1. Nepheline hydrate 1 can be crystallized from glass of NaAlSiO_4 composition only; any excess silica inhibits crystal growth. Since normal alkaline rocks contain more silica than end-member nepheline, the rare occurrence of nepheline hydrate 1 as a mineral can be explained (Saha, 1961).

Morey and Fournier (1961) examined the hydrothermal decomposition of nepheline. Details of their experiment are given in Table 9. Nepheline with the composition of SiO_2 - 42.34 percent, Al_2O_3 - 34.22 percent, Fe_2O_3 - 0.06 percent, CaO - 0.45 percent, Na_2O - 15.73 percent, K_2O - 6.45 percent, H_2O^+ - 0.28 percent and H_2O^- - 0.06 percent was placed in a column, and water at 295°C and 1.6 Kbar was pumped through it. The pH of the water was initially 5.8. The pH and

Table 7. Potassium-Argon ages of Nephelines from Ontario, Canada (modified from McIntyre et al., 1966)

Locality	Age (m. y.)
Princess Quarry, Ontario	904
Goulding-Keene Quarry, Ontario	879, 903
Gill Quarry, Ontario	1003, 992
Blue Mountain, Ontario	1007
Bigwood Twp., Ontario	1169, 1144

Table 8: Nepheline Alteration Products

Nepheline Alteration Products	Authors
alkali feldspar ($\text{NaAlSi}_3\text{O}_8$)	Moyd (1949)
*analcite ($\text{NaAlSi}_2\text{O}_6$)	Winchell & Winchell (1967) Morey & Fournier (1961) Saha (1961)
Boehmite (AlO_2H)	Morey & Fournier (1961)
Cancrinite ($\text{Na}_3\text{Ca}(\text{AlSiO}_4)_2\text{CO}_3$)	Winchell & Winchell (1967) Moyd (1949)
Colloid	Winchell & Winchell (1967)
Corundum (Al_2O_3)	Moyd (1949)
Diaspore (AlO_2H)	Dunham (1933) Thugutt (1932)
garnet ($\text{A}_3\text{B}_2(\text{SiO}_4)_3$)	Winchell & Winchell (1967)
Halloysite	Huang (1974)
"hydronepheline"	Barrer & White (1952) Jeremine (1948) Dunham (1933) Tilley & Harwood (1931)
Kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$)	Huang (1974) Winchell & Winchell (1967)
Muscovite ($\text{KA1}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$)	Winchell & Winchell (1967) Morey & Fournier (1961) Moyd (1949)
*Natrolite ($\text{Na}_2\text{Al}(\text{AlSi})_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$)	Winchell & Winchell (1967) Saha (1961) Ofstedahl (1952) Moyd (1949) Thugutt (1945a, 1932) Dunham (1933)

Table 8: Nepheline Alteration Products (Continued)

Nepheline Alteration Products	Authors
Nepheline hydrate I ($\text{NaAlSiO}_4 \cdot 1/2\text{H}_2\text{O}$)	Saha (1961) Barrer & White (1952)
Paragonite ($\text{NaAl}_2(\text{Al},\text{Si})_3\text{O}_{10}(\text{OH})_2$)	Morey & Fournier (1961) Saha (1961)
*phillipsite ($(\text{Ca},\text{K}_2,\text{Na}_2)_5\text{Al}_{10}\text{Si}_{22}\text{O}_{64} \cdot 20\text{H}_2\text{O}$)	Winchell & Winchell (1967) Thugutt (1945a)
Plagioclase (An ₆₇), ((Ca _{.67} Na _{.33})Al _{1.67} Si _{2.33} O ₈)	Kutty <u>et al.</u> , (1969)
*Sodalite ($\text{Na}_8(\text{AlSi})_6\text{O}_{24} \cdot (\text{Cl}_2, \text{SO}_4)$)	Winchell & Winchell (1967) Moyd (1949)
*thomsonite ($\text{Na}_4\text{Ca}_8(\text{AlSi})_{20}\text{O}_{80} \cdot 24\text{H}_2\text{O}$)	Winchell & Winchell (1967) Thugutt (1945b) Tilley & Harwood (1931)

*Zeolite minerals

Table 9: Nepheline Experimental Data (Morey and Fournier, 1961).

	SiO ₂	Al ₂ O ₃	K ₂ O	Na ₂ O	Total
Average solubility in ppm for first 33 days and 22 collections.	200	148	30	113	491
Average solubility in ppm for last 102 days and 39 collections	188	118	24	86	416
Average solubility in ppm for total of all runs.*	192	127	26	95	440

Grams dissolved in the first 33 days	0.793	0.587	0.121	0.450	1.951
Grams dissolved in the last 102 days	1.662	1.040	0.215	0.762	3.679
Total grams dissolved	2.455	1.627	0.336	1.212	5.630

Mole ratios for first 33 days	2.29	1.00	0.22	1.26	--
Mole ratios for the last 102 days	2.66	1.00	0.22	1.21	--
Mole ratios for the total	2.57	1.00	0.22	1.25	--

Temperature: 295 ± 5°C	Initial sample weight: 8.453 gm				
Pressure: 1.6 ± .1 kbar	Weight of liquid pumped over sample:				
Duration: 135 days	First 33 days - 3969 gm				
	Last 102 days - 8,829 gm				
	total - 12,798 gm				

* Calculated by dividing the total grams dissolved by the total amount of liquid pumped over the sample.

concentration gradients inside the column controlled the deposition of the different alteration products. After 135 days, 67 percent of the original nepheline had dissolved. Muscovite (a mica) and analcite ($\text{NaAlSi}_2\text{O}_6$, a zeolite) were identified as alteration products at the column exit. Boehmite ($\text{AlO}(\text{OH})$), paragonite (a mica) and muscovite were identified at the column entrance. Muscovite and boehmite were identified in the middle of the column.

NEPHELINE GROUP

Structure

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POLLUCITE: $\text{CsAlSi}_2\text{O}_6 \cdot n\text{H}_2\text{O}$

Pollucite differs from the supercalcine phase in that it is hydrated. Pollucite has a structure which is similar to analcime, $\text{NaAlSi}_2\text{O}_6$, a zeolite. Pollucite is not stable at surface conditions. It occurs in certain types of granitic pegmatites.

MINERAL DATA

Mineral data for pollucite are as follows:

Formula: $(\text{Cs}, \text{Na})\text{AlSi}_2\text{O}_6 \cdot n\text{H}_2\text{O}$

Crystal System:	Cubic
Space Group:	Ia3d
Z:	16
Lattice Constant:	$a = 13.64 - 13.74 \text{ \AA}$
Mohs Hardness:	6.5 - 7
Density (gm/cm^3):	2.35 - 3.03 meas., 2.94 calc.

STRUCTURE

Pollucite is a tektosilicate related to the zeolite group, Figure 9. The framework has a disordered silicon and aluminum occupancy in the tetrahedral sites. All of the tetrahedral sites are symmetry related. The framework contains a set of sixteen large cavities at $1/8, 1/8, 1/8$ which form channels parallel to the body diagonals of the cubic cell. The sixteen large cavities are occupied by twelve Cs^+ ions and four H_2O molecules in a disordered manner. Each Cs^+ ion is coordinated by twelve oxygens, six of the Cs-O interatomic distances are 3.40 Å and six are 3.57 Å. The Na^+ ions occupy four of twenty-four symmetry related sites at $1/4, 1/8, 0$. Most sodium ions are coordinated by two water molecules and four framework oxygens, while most water molecules coordinate with two sodium ions (Beger, 1969).

CHEMISTRY

Pollucite is the only major cesium mineral, containing up to 35 percent Cs_2O . Pollucite forms a series with analcime ($\text{NaAlSi}_2\text{O}_6$) by replacement of cesium at $1/8, 1/8, 1/8$, by H_2O and the simultaneous addition of sodium ions at $1/4, 1/8, 0$ to maintain charge neutrality. Natural pollucites complete the series except for $\text{POLL}_{55} - \text{POLL}_{62}$ and $\text{POLL}_{82} - \text{POLL}_{100}$ (Cerny, 1974). Cerny (1974) proposed a nomenclature for the series: analcime ($\text{POLL}_0 - \text{POLL}_5$), cesian analcime ($\text{POLL}_5 - \text{POLL}_{50}$), sodian pollucite ($\text{POLL}_{50} - \text{POLL}_{95}$) and pollucite ($\text{POLL}_{95} - \text{POLL}_{100}$). This report will use pollucite to mean any member in the series. Few complete analyses of pollucites are available because of the limited number of occurrences. Cerny (1974) has tabulated all the complete analyses of pollucite in the literature up to 1974, Table 10.

A persistent and constant deviation in the Si/Al ratio from the idealized value of 2 is observed in natural specimens. According to Cerny (1974), values are well centered around 2.33 and two thirds

Table 10: Chemical Analyses and Physical Properties of Sodion Pollucite.
Compositions are expressed as atoms per unit cell (Cerny, 1974).

	1	2	3	4	5	6	7	8	9	10
Si	2.075		2.127	2.095	2.061	2.095	2.101	2.138	2.084	2.106
Al	.916		.861	.883	.937	.929	.894	.870	.888	.913
Fe ³⁺	.004		-	.010	-	-	tr.	-	.027	.002
ΣR ⁺⁴	2.995		2.988	2.988	2.998	3.024	2.995	3.008	2.999	3.021
Na	.298 (4.47)		.357	.261	.181	.248	.164	.211	.204	.110
Cs	.465 (23.10)		.445	.494	.551	.590	.595	.600	.634	.590
Rb	.036 (.03)		-	-	.017	.016	.047	-	-	.024
K	.027 (.48)		.009	.055	.103	.029	.029	.035	.011	-
Li	.058		.015	.072	.028	-	.038	-	-	.036
Mg	.012		-	-	-	-	-	-	-	.012
Ca	.017 (.05)		.004	.026	.001	-	-	-	.036	.021
Mn	-		-	-	-	-	-	-	-	-
Σ cat.	.913		.830	.908	.881	.883	.873	.846	.885	.793
H ₂ O	.16		.54	.40	.41	.41	.27	.36	.41	.23
Si/Al	2.27		2.47	2.37	2.19	2.25	2.35	2.45	2.35	2.31
Poll*	50.9	51.3	53.5	54.4	62.5	66.8	66.8	70.9	71.7	74.2
(A)	-	-	13.64	-	13.674	-	-	-	-	-
density	-	2.73	2.68	-	-	2.865	2.917	2.890	2.896	2.94

*Poll = Cs x 100/(Cs+Li+Na+K+Rb+Ca+Mg+Mn)

() wt. % of oxides

1. Far East (Vlasov et al., 1964)
2. Puklice (Miskovsky 1960; new data given here)
3. Greenwood B (Richmond and Gonyer 1938)
4. Kalbinski Range (Ginzburg 1946)
5. Nagatare (Sakurai et al., 1972)
6. Karibib (Nel 1944)
7. Varutrask (Quensel 1937)

8. Elba (Rammelsberg, quoted in Wells 1891)
9. Elba (Gossner and Reindl 1932)
10. Sayan Mts. (Melentjev 1961)
11. Leominster (Richmond and Gonyer 1938)
12. Jeclov (Miskovsky 1960)
13. Maine (Newnham 1967)

Table 10: Chemical Analyses and Physical Properties of Sodion Pollucite.
Compositions are expressed as atoms per unit cell (Cerny, 1974)
(continued)

	11	12	13	14	15	16	17	18	19	20
Si	2.088	2.119	-	2.072	2.061	2.140	2.131	2.071	2.124	2.092
Al	.924	.869	-	.918	.940	.851	.868	.944	.900	.909
Fe ⁺³	-	.002	-	-	-	-	-	tr.	.003	-
Er ⁺⁴	3.012	2.990	-	2.990	3.001	2.991	2.999	3.030+	3.027	3.001
Na	.182	.172 (2.0)		.166	.192	.163	.171	.143	.118	.146
Cs	.658	.647 (32.0)		.732	.728	.747	.687	.628	.615	.722
Rb	-	- (.2)		-	-	.031	.014	.021	-	-
K	.036	.036 (.2)		.030	.002	.004	.006	tr.	-	.023
Li	-	-	-	.008	.015	.010	-	.002	.014	-
Mg	-	-	-	-	-	-	-	-	.007	-
Ca	-	-	-	.011	-	-	.002	-	.014	.001
Mn	-	-	-	-	-	-	-	.001	-	-
Σcat	.876	.855	-	.947	.937	.955	.880	.796	.768	.89
H ₂ O	.31	.37 (1.8)		.24	.25	.23	.23	.29	.16	.25
Si/Al	2.26	2.44	-	2.26	2.20	2.51	2.45	2.20	2.36	2.30
Poll*	74.9	75.7	75.8	77.3	77.6	78.2	78.4	78.9	80.1	80.5
a (Å)	13.65	-	13.682	-	-	13.66	-	13.688	-	13.65
sp. gr.	2.89	2.896	2.94	2.981	2.94- 3.03	2.88	-	2.832	-	2.97

14. Hebron (Wells (1851)

15. Rumford (Foote 1898, quoted in
Gossner and Reindl 1932)

16. Bernic Lake (Nickel 1961)

17. Buckfield (British Museum, Natural
Sciences Lab. No. 3487)

18. Luolamaki (Neuvonen and Vesasalo
1960)

19. Northwestern European U.S.S.R. (Sosedko
1954, quoted in Melentjev 1961)

20. Greenwood A (Richmond and Gonyer 1938)

Figure 9: Projection on (001) of the aluminosilicate framework and the cesium and water positions in pollucite. The lower halves of four unit cells are shown, cesium and water are represented by solid circles at $1/8 \underline{c}$ and stippled circles at $3/8 \underline{c}$ respectively (Beger, 1969).

fall between 2.22 and 2.44. The tetrahedral framework composition $\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$ can be considered typical for the whole series, Cerny (1974).

Figure 10 shows the atomic contents of Cs^+ plotted against those of Na^+ plus other minor cations. The data follow the line connecting the 0.9 points in accordance with the -0.9 anionic charge. Deviations are caused by slight variation in the Si/Al ratio and deficiencies in cations, common in zeolite group minerals, Cerny (1974).

Nel (1944) and Neuvonnen and Vesasalo (1960) proposed rules which relate Cs^+ , Na^+ , H_2O , Al^{+3} and Si^{+4} contents for members of the analcime-pollucite series. More recently, Cerny (1974) summarized stoichiometric relationships for the analcime-pollucite series as: $(\text{Cs}^+) + (\text{H}_2\text{O}) = 1$, $(\text{H}_2\text{O}) > (\text{Na}^+)$, $(\text{Si}/\text{Al}) > 2$ and $(\text{Al}) < 1$.

Ahrens (1945, 1947) has examined minor constituents in five natural specimens, Table 11. Small amounts of Ga^{+3} have been found to substitute for Al^{+3} of the framework in pollucites. The large ions Ti^+ , K^+ and Rb^+ substitute for cesium. Of the three, rubidium is the most abundant. Pollucite sometimes is a major carrier of rubidium. Small size ions determined are Li^+ , Mg^{+2} , Ca^{+2} and Mn^{+2} . These ions may substitute for cesium, sodium or may be interstitial ions in the large cavities. Natural pollucites do not contain significant amounts of intermediate-size ions such as Ba^{+2} .

The water in pollucites can be removed upon heating, but anhydrous pollucite does not absorb water as readily as other zeolite minerals. Steric hinderence from the large alkali ions (mainly Cs^+) may account for this observation. Supercalcine pollucite is anhydrous.

OCCURRENCE

Members of the analcime-pollucite series vary in abundance and occurrence. Analcime, the most abundant, occurs as a low temperature mineral in siltstones, sandstones and other sedimentary rocks; as an amygdale mineral in basaltic flows; and uncommonly as a minor

Figure 10: Atomic contents of Cs plotted against those of Na plus all minor cations (ΣNa). Most data follow very closely the line connecting $\text{Na}_{0.90}$ and $\text{Cs}_{0.90}$ in accordance with the average tetrahedral Al content of 0.90 (Cerny, 1974).

Table 11: Minor Constituents of Five Pollucites (Ahrens, 1945, 1947).

	Weight Percent				
	Tl ₂ O	Rb ₂ O	Li ₂ O	Ga ₂ O ₃	K ₂ O
Okongaua Ost 72 Karibib, South West Africa	0.011	0.54	0.021	0.0012	0.49
Norway	0.0013	0.23	---	0.0012	0.76
Greenwood, Maine	0.0019	0.68	0.008	0.0005	0.16
Tin Mountain, south Dakota	0.0019	0.25	0.006	0.0005	0.19
Varutrask, Sweden	0.008	0.37	0.053	0.0010	2.5

constituent in metamorphic and plutonic rocks.

Cesian analcime and sodian pollucite are restricted to highly differentiated complex lithium-rich granitic pegmatites. Cesium's large ionic size and very low crustal abundance limits cesium mineral formation to complex pegmatites, where volatile fractionation has increased the cesium content to a high value. The preference of the smaller rubidium ion in the early minerals during pegmatite crystallization further fractionates cesium until the late stages.

Sodian pollucite and cesian analcime occur in complex lithium pegmatite districts in several places in the United States and throughout the world. Undoubtedly these minerals occur in more districts, but their recognition is very difficult, and consequently often overlooked. The cesium rich end-member of the pollucite-analcime series is not known to occur in nature.

ALTERATION

Pollucite weathers by the removal of Cs^+ , Rb^+ and K^+ , and alters to clays. Cerny (1978) has identified illite + kaolinite + smectites in clay pods derived from large pollucite crystals in Manitoba pegmatites. Kaolinite and montmorillonite have been identified as alteration products by Miskovsky (1955, 1960), Ginzburg (1946), Quensel (1956) and Neuvonen and Vesasalo (1960). Vlasov (1964) states that the removal of cesium from pollucite is rapid, and the cesium content will even substantially diminish in samples in tailings piles. "W.L. Roberts has observed pollucite from the Tin Mountain pegmatite, South Dakota, transforming to montmorillonite after 6 months exposure to surface conditions" Cerny (1978). Cerny (1978) has determined 0.24 percent Cs_2O residual in clays derived from pollucite. Much of the alteration of pollucite, particularly that observed by Cerny in the Manitoba pegmatites, is caused in part by the highly reactive replacing fluids left during the final stages of pegmatite crystallization. This implies temperatures less than 400°C with attendant fluids enriched in H_2O and CO_2 .

Pollucite frequently is veined by albite ($\text{NaAlSi}_3\text{O}_8$), lepidolite (a mica), lithium micas, spodumene ($\text{LiAlSi}_2\text{O}_6$) and mechanical mixtures of these minerals with clays (Quensel, 1938; Cerny, 1978). These vein minerals are derived from the residual pegmatite fluids active during the replacement period of crystallization of a complex pegmatite. Most veins represent products of fracture fillings and are not alterations of the pollucite. Pollucite may be replaced by other minerals: quartz, aplitic albite, apatite ($(\text{Ca}_5(\text{PO}_4)_3\text{OH})$) and lepidolite (a mica) have been noted (Vlasov, 1964).

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SCHEELITE GROUP: Ca(W,Mo)O_4

Scheelite (CaWO_4) and rare powellite (CaMoO_4) are analogues for supercalcine "scheelite", $(\text{Ca,Ba,Sr})\text{MoO}_4$. SrMoO_4 and BaMoO_4 are not known as minerals. CaWO_4 and CaMoO_4 are durable.

MINERAL DATA

Mineral data for scheelite and powellite are as follows:

Formula:	Scheelite (CaWO_4)	Powellite (CaMoO_4)
Crystal System:	Tetragonal	Tetragonal
Space Group:	$I4_1/a$	$I4_1/a$
Z:	4	4
Lattice Constants:	$a = 5.257 \text{ \AA}$ $c = 11.371 \text{ \AA}$	$a = 5.23 \text{ \AA}$ $c = 11.44 \text{ \AA}$
Mohs Hardness:	4 1/2 - 5	3 1/2 - 4
Density (gm/cm^3):	6.10 meas. 6.12 calc.	4.23 meas. 4.26 calc.

STRUCTURE

In this paper, the term scheelite refers to CaWO_4 , a mineral and not to the supercalcine "scheelite" phase, $(\text{Ca},\text{Sr})\text{MoO}_4$. SrMoO_4 should have a very similar crystal chemistry to powellite (CaMoO_4) and scheelite.

The ABO_4 molybdates and tungstates of calcium, barium and strontium crystallize in the tetragonal scheelite structure, space group $I4_1/a$, Figure 11. There are four ABO_4 formulas in the body centered unit cell. Both the A and B atoms occupy special positions on $\bar{4}$ axes while the oxygen atom occupies a general position. A is a divalent ion while B is Mo^{+6} or W^{+6} . Each A^{+2} ion is surrounded by eight B^{+6} cations and four A^{+2} cations. Four of the B^{+6} cations form the corners of a square whose center is the A^{+2} ion. This square is parallel to the basal plane. The other four B^{+6} ions are located at the corners of a tetrahedron whose center is the A^{+2} ion. Four A^{+2} ions are also located at the corners of a tetrahedron whose center is the A^{+2} ion. Each B^{+6} ion is surrounded by an analogous arrangement of eight A^{+2} and four B^{+6} ions.

Symmetry considerations require that all B-O distances be equal and that there be only two different A-O distances. BO_4^{-2} tetrahedra are slightly compressed along the c axis, Figure 11, (Gurmen, Daniels and King, 1971).

Lattice parameters and cell volumes are listed in Table 12. For the scheelite structure, the cell volumes of the molybdates are smaller than the corresponding tungstates.

The scheelite structure is related to the wolframite (monoclinic CaWO_4) structure. In both structures the oxygen atoms are coordinated by three cations. The wolframite structure has one half of the oxygen atoms coordinated to two A cations and one half coordinated to two B cations while the scheelite structure has each oxygen coordinated to one B and two A cations (Sleight, 1972). Therefore, both A and B cations in the wolframite structure are coordinated by six oxygen atoms. In contrast, the A and B cations in

Figure 11: Two unit cells of the ABO_4 scheelite structure. (Cockayne and Hollox, 1964).

Table 12: Cell Dimensions of ABO_4 Compounds with the Scheelite Structure.

Compound	$V(\text{\AA}^3)$	a	c	Density (gm/cm^3)
1. CdMoO_4	297.47	5.155	11.194	6.08
2. CaWO_4 scheelite	313.94	5.25	11.39	6.09
3. CaMoO_4 powellite	312.27	5.226	11.434	4.255
4. SrWO_4	350.66	5.4168	11.951	6.353
5. SrMoO_4	349.78	5.3944	12.020	4.700
6. BaWO_4	400.81	5.6134	12.720	6.382
7. BaMoO_4	399.23	5.5802	12.821	4.945
8. PbWO_4 stolzite	359.45	5.4619	12.049	8.408
9. PbMoO_4 wulfenite	357.72	5.435	12.11	6.815
10. EuWO_4	349.47	5.411	11.936	

JCPDS File Number:

1. 7-209	6. 8-457
2. 8-145	7. 29-193
3. 29-351	8. 19-708
4. 8-490	9. 8-475
5. 8-482	10. 22-1101

the scheelite structure are in eight-fold and four-fold coordination with oxygen atoms, respectively.

Nicol and Durana (1971) suggest that scheelite, CaWO_4 , transforms to the monoclinic wolframite structure at 12 Kbars, powellite, tetragonal CaMoO_4 , at 27 kbars.

CHEMISTRY

Continuous solid solution occurs between end members scheelite (CaWO_4) and powellite (CaMoO_4). Isomorphism in the scheelite crystal structure is of the ion for ion and block type (Kononov, 1967). In molybdenum bearing scheelite, the distribution of Mo appears to be disordered with low Mo concentration and ordered with higher Mo concentrations. As its concentration increases to 16.81 percent CaMoO_4 , three dimensional blocks of powellite are detected.

Complete solid solutions are observed in the systems CaWO_4 - SrWO_4 and CaWO_4 - PbWO_4 . Fairly extensive solid solution occurs in the Ba-rich side of the system CaWO_4 - BaWO_4 and in the CaWO_4 - CdWO_4 system. In the scheelite-wolframite systems CaWO_4 - MnWO_4 , CaWO_4 - MgWO_4 , CaWO_4 - ZnWO_4 , and CaWO_4 - NiWO_4 , only CaWO_4 - MnWO_4 has a significant range of solid solution (Chang, 1967), Table 13. Unit cell volumes in the systems CaWO_4 - SrWO_4 , CaWO_4 - PbWO_4 , and CaWO_4 - CdWO_4 increase with increasing content of SrWO_4 , PbWO_4 and CdWO_4 respectively.

Substitution of a divalent A cation by a trivalent rare earth in the ABO_4 scheelite structure with no substitution of Mo or W is possible by two means. The substitution can be made by the formation of vacant atomic positions leading to a defect structure with the general formula $\text{R}_2^{+3}(\text{BO}_4)_3$, or the vacant atomic positions can be filled by a univalent cation resulting in compounds of the $\text{A}^{+1}\text{R}^{+3}(\text{BO}_4)_2$ type (where A = alkali cation, R = rare earth, and B = W or Mo). Chang (1969) studied the effect of La and Sm substitution in CaWO_4 ; the two rare earths representing the minimum and maximum differences in ionic size with calcium. Sodium was chosen as the

Table 13: Summary of Phase Diagrams. Ex.: 10 mole percent CaWO_4 is soluble in CdWO_4 at 1100°C ; 55 percent CdWO_4 is soluble in CaWO_4 at 1100°C . The lattice parameters a_o , c_o are reduced with increasing CdWO_4 . (Chang, 1967, 1969).

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	CdWO_4 (mol %)	SrWO_4	PbWO_4	BaWO_4	MnWO_4
CaWO_4	10	complete	complete	10	2.5
(mol. %)	55	solid	solid	(1150°)	
		solution	solution	2.5	10
				(1100°)	
$T^\circ\text{C}$	1150°	$\geq 825^\circ$	$\geq 815^\circ$	1150°	1100°
<hr/>					
-----	MgWO_4	$\text{La}_2(\text{WO}_4)_3$	$\text{Sm}_2(\text{WO}_4)_3$	$\text{NaLa}(\text{WO}_4)_2$	$\text{NaSm}(\text{WO}_4)_2$
CaWO_4	-limited solid	complete	complete	complete	complete
	solution	solid	solid	solid	solid
	2	solution	solution	solution	solution
$T^\circ\text{C}$	110°	1020°	1020°	825°	825°

univalent cation. He found solid solutions in the systems CaWO_4 - $\text{La}_2(\text{WO}_4)_3$ and CaWO_4 - $\text{Sm}_2(\text{WO}_4)_3$ form above 1020°C and in each system a phase boundary separates tetragonal scheelite and the monoclinic defect scheelite, Figure 12. In the systems CaWO_4 - $\text{NaLa}(\text{WO}_4)_2$ and CaWO_4 - $\text{NaSm}(\text{WO}_4)_2$ continuous solid solutions form above 825°C , and phase changes are not detected. The ternary system CaWO_4 - $\text{NaLa}(\text{WO}_4)_2$ - $\text{La}_2(\text{WO}_4)_3$ at 750°C exhibits three phase regions, at 900°C two phase regions dominate, and at 1025°C one phase regions are present, the tetragonal solid solution transforms to a monoclinic solid solution with increasing amounts of $\text{La}_2(\text{WO}_4)_3$, Figure 13 (Chang, 1969). Lattice parameters increase with increasing $\text{La}_2(\text{WO}_4)_3$.

OCCURRENCE

Scheelite (CaWO_4) occurs in pneumatolytic or hydrothermal deposits, pegmatites, ore veins associated with granite and gneiss, contact metamorphic deposits and placers. Tactites are the major contact metamorphic rock type. Quartz, calcite and occasional rare minerals are associated with vein deposits; beryl and fluorite are common associations in pegmatites (Hsu and Galli, 1973). Depositional temperatures range from 100° to 500°C (Kelley and Turneare, 1970); Tugarinov and Naumov, 1972; Foster, 1977). Powellite (CaMoO_4) is formed by the oxidation of molybdenite (MoS_2), which is commonly associated with scheelite. Relatively pure powellite (CaMoO_4) occurs in vugs and as pseudomorphs after molybdenite. BaMoO_4 and SrMoO_4 have not been reported as minerals. The mineral association of the scheelite-powellite series in pegmatites, hydrothermal veins and contact metasomatic rocks is shown in Table 14.

Compositional variations of the scheelite-powellite series are not uniform as shown by the histogram in Figure 14a (Hsu, 1977). Most natural scheelites contain less than 1 mole percent powellite (CaMoO_4), the majority being of pegmatite and hydrothermal origin. The pure scheelites tend to associate with molybdenite when

Figure 12: Phase relations in the CaWO_4 - $\text{La}(\text{WO}_4)_3$ and CaWO_4 - $\text{Sm}_2(\text{WO}_4)_3$ systems. Open circles = one phase, scheelite; solid circles = one phase, defect-scheelite, (Chang, 1969).

Figure 13: Phase relations in the system $\text{CaWO}_4 - \text{La}_2(\text{WO}_4)_3 - \text{NaLa}(\text{WO}_4)_2$. The open circles = tetragonal scheelite, solid circles = monoclinic defect scheelite, left half shaded = two tetragonal phases, and right half shaded = one tetragonal and one monoclinic phase, and triangles = two tetragonal and one monoclinic phase (Chang, 1969). Note: it is possible that considerable amounts of sodium (and rare earths) are present in supercalcine "scheelite".

Table 14: Mineral Associations of Various Occurrences of the Scheelite-Powellite Series (Hsu and Galli, 1973)

Mineral	Major (30%)		Minor (30 - 5%)		Accessory (5 - 1%)		Trace (1%)	
	A	B	A	B	A	B	A	B
Actinolite	--	*	--	*	--	*	--	*
Apatite	--	--	--	--	--	--	*	*
Bertrandite	--	--	--	--	--	--	*	--
Beryl	--	--	--	--	*	--	*	--
Biotite	--	--	--	--	--	*	--	*
Calcite	*	*	*	*	*	*	*	*
Chalcopyrite	--	--	--	--	--	*	--	*
Chlorite	--	--	--	*	*	*	*	*
Cinnabar	--	--	--	--	--	--	*	--
Cuproscheelite	--	--	*	--	--	--	--	--
Dolomite	--	--	--	--	--	*	--	--
Epidote	--	*	--	*	*	*	--	--
Fluorite	--	*	*	*	*	*	*	--
Galena	--	--	--	--	--	--	*	*
Garnet	--	*	--	*	--	*	--	--
Hematite	--	--	--	--	--	--	*	*
K-feldspar	*	--	*	--	--	*	--	--
Magnetite	--	--	--	*	*	*	*	*
Molybdenite	--	--	--	*	--	*	--	*
Muscovite	*	--	*	--	*	--	*	*
Phenacite	--	--	--	--	*	--	--	--
Plagioclase	*	--	--	--	--	--	--	--
Pyrite	--	--	--	*	*	*	*	*
Pyroxene	--	*	--	*	--	*	--	*
Pyrrhotite	--	--	--	*	--	*	--	*
Quartz	*	*	*	*	*	*	--	--
Seapolite	--	--	--	--	*	--	--	--
Sphalerite	--	--	--	--	--	--	*	*
Sphene	--	--	--	--	--	--	--	*
Stilbite	--	--	--	*	--	*	--	--
Talc	--	--	--	--	--	*	--	--
Tetrahedrite	--	--	--	--	--	--	*	*
Tourmaline	--	--	*	--	*	--	--	--
Tremolite	--	*	--	--	*	*	--	--
Scheelite-Powellite	*	--	*	*	*	*	--	*

A: In pegmatites and hydrothermal veins.

B: In contact-metasomatic rocks.

(a)

(b)

Figure 14: (a) A histogram showing frequency of occurrence plotted against composition for members of the scheelite-powellite solid solution series (Hsu, 1977).

(b) A diagram indicating the stability field for coexisting scheelite and powellite and 577°C and 1 kbar fluid pressure (Hsu, 1977).

molybdenum is available. Pure powellite and tungstenite are rare, and the association of powellite and tungstenite in nature has not been reported (Hsu, 1977). This is explained by the stability fields of scheelite, tungstenite, powellite and molybdenite, Figure 14b. The diagram illustrates the common association of scheelite and molybdenite (MoS_2) in tactite deposits. Powellite requires a high oxygen fugacity for stability. Molybdscheelite also forms in an oxidizing environment; a reducing environment favors pure scheelite and molybdenite. The formation of molybdenite instead of powellite is supported by the thermodynamic equation based on data of Robie and Waldbaum (1968) at 1 atm. and 25°C:

This reaction will proceed to the right and molybdenite (MoS_2) formation will be favored over powellite (CaMoO_4) under normal crustal conditions.

Pure scheelite in hydrothermal veins and hydrothermally altered rocks not associated with molybdenite may be due to the rarity of molybdenum in the ore solutions (Hsu and Galli, 1973).

Yttrium is concentrated in the scheelite-powellite series of hydrothermal origin and may be of the form $\text{Na} + \text{Y}$ substituting for 2Ca^{+2} as discussed earlier. The availability of Na^+ in hydrothermal solutions facilitates this type of substitution (Hsu and Galli, 1973).

ALTERATION

Powellite (CaMoO_4) is both an uncommon and unimportant ore mineral in comparison with scheelite. Therefore alteration of powellite has not received as much study as scheelite alteration.

Scheelite (CaWO_4) is practically insoluble in pure water at elevated temperatures. Scheelite solubility at $P(\text{H}_2\text{O}) = 1000$ bars, 265°C and 450°C is 1 ppm and 6.6 ppm, respectively. Solubility is enhanced in solutions containing KCl buffered with the assemblage: quartz, K-feldspar, and muscovite (Foster, 1977). CaMoO_4 is more soluble than CaWO_4 . At constant temperature the solubilities of both

increase with chloride concentration. Both CaMoO_4 and CaWO_4 have positive temperature coefficients of solubility. At 350°C the limit of solubility of CaMoO_4 in 39 wt % NaCl is 0.016 wt. % (160 ppm)(Yastrebova et al., 1963).

Hydrothermal alteration of tungsten minerals is not often reported in the geologic literature. Scheelite alteration has been studied by Heier (1955), Bryzgalin (1958), Oelsner (1954), and Magnee and Aderca (1960).

Tungsten minerals appear to be slowly attacked by acid surface waters, especially by strongly acidic waters of weathering sulfide deposits (Newhouse, 1934). Gannet (1919) indicates that alkaline solutions in nature probably have little effect on tungsten minerals. Movement of tungsten and molybdenum in near surface solutions is shown by the existence of haloes in soils around ore deposits (Krainov et al., 1965).

The scarcity of tungsten placers is commonly explained by the brittleness of scheelite and wolframite, which leads to their mechanical breakdown and dispersion (Krauskopf, 1970). So far as alteration and weathering characteristics are concerned scheelite (CaWO_4) may not be a suitable natural analogue for supercalcine "scheelite", $(\text{Ca},\text{Sr})\text{MoO}_4$.

SCHEELITE

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SODALITE GROUP: $(\text{Na,Ca})_{4-8}(\text{AlSiO}_4)_6(\text{S,SO}_4\text{Cl}_2)_{1-2}$

Sodalite group minerals are isostructural with the supercalcine sodalite phase, $\text{Ca}_2\text{Na}_6(\text{AlSiO}_4)_6(\text{MoO}_4)_2$. Sodalite is a zeolite. It occurs in silica undersaturated rocks and is not durable.

MINERAL DATA

Mineral data for sodalite minerals are as follows:

Formula:	Sodalite $\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{Cl}_2$	Nosean $\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{SO}_4$
Crystal System:	Cubic	Cubic
Space Group:	$\overline{\text{P}}43\text{m}$	$\overline{\text{P}}43\text{m}$
Z:	1	1
Unit Cell Parameter:	$a = 8.877 - 8.91 \text{ \AA}$	$a = 9.05 - 9.114 \text{ \AA}$
Mohs Hardness:	5.5 - 6	5.5
Density (gm/cm^3):	2.14 - 2.4 meas. 2.27 - 2.33 calc.	2.22 - 2.4 meas. 2.205 - 2.34 calc.

STRUCTURE

The crystal structure of the sodalite group was determined by Pauling (1930) and Barth (1927), Figure 15. The sodalite group members are zeolites with frameworks in which aluminum and silicon are surrounded by nearly undistorted tetrahedra of oxygen. The tetrahedra share all of their corners with other tetrahedra to form an open framework with cubo-octahedral voids whose centers are occupied by anions. The cubo-octahedral voids are bound by six rings of four tetrahedra parallel to (100) and eight rings of six tetrahedra parallel to (111). Each cage shares faces with eight other cages. The sodium ions lie on threefold rotation axes and are surrounded by four anions; three framework oxygen ions and one sulfate, chloride or sulfide. Non-framework anions are surrounded by four sodium ions. The cubo-octahedral cages are centered at (0,0,0) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Sodalite ($\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{Cl}_2$) has an ordered arrangement of silicon and aluminum ions while nosean ($\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{SO}_4)$) is probably disordered, Schulz and Saalfeld (1965). The structures of hauyne ($((\text{Na}, \text{Ca})_{4-8}\text{Al}_6\text{Si}_6\text{O}_{24}(\text{SO}_4, \text{S})_{1-2})$) and lazurite ($((\text{Na}, \text{Ca})_8(\text{Al}, \text{Si})_{12}\text{O}_{24}(\text{S}, \text{SO}_4))$) have not been refined.

All minerals of the sodalite group have similar structures. Nosean has a less collapsed framework than sodalite due to substitution of Cl^- by the more bulky sulfate ion. Hauyne contains more sulfate than nosean and therefore has a more expanded framework. Variation in unit cell is due chiefly to the size of the nonframework anion and to a lesser extent to the size of the nonframework cations (Taylor, 1972, 1975). Pauling (1930) calculated 9.4 Å as the size of the fully expanded framework unit cell.

Thermal expansion of the sodalite group minerals has been examined by Taylor (1968, 1972). Thermal expansion curves for nosean and hauyne have the same form, Figure 16. An initial rapid increase in unit cell volume continues from room temperature up to an inflexion at 450 to 700°C, followed by a more gradual linear increase. The rapid initial increase in unit cell size is attributed to rotation of

Figure 15: Schematic diagram for the partially collapsed (right) and fully expanded structures (left) of sodalite. Only the framework tetrahedra are shown (Taylor, 1972).

Figure 16: Thermal expansion curves for (a) four noseans, (b) five hauynes and (c) one sodalite (Taylor, 1968).

the silicon and aluminum tetrahedra. The maximum framework expansion is believed to occur at the inflexion. The different inflexion temperatures for different samples may reflect slightly varying Si:Al ratios. The more gradual expansion following the inflexion is due to lengthening of Si-O and Al-O framework bonds. The thermal expansion curve for sodalite shows no inflexion up to 920°C, suggesting that full expansion of the structure is not achieved in this temperature range.

CHEMISTRY

Sodalite ($\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{Cl}_2$) is the most sodium-rich and chlorine-rich mineral of the sodalite group of zeolite minerals. The total sodium content varies slightly due to substitution by calcium and potassium. Minor substitution of ferric iron for aluminum occurs. In hackmanite, a fluorescent variety of sodalite, small amounts of sulfide substitute for chloride. Small amounts of water probably substitute for chlorine. Hydrosodalite, a synthetic zeolite, is structurally and chemically similar to sodalite except for essential water. Natural hydrosodalite has not been reported. Fellenberg and Lunde (1926) reported a sodalite bearing 2.87 weight percent molybdenum. Supercalcine sodalite is thought to be a molybdate. Sorensen (1960) described a beryllium containing sodalite (in alumino-silicates, beryllium usually substitutes for aluminum).

Nosean ($(\text{Na},\text{Ca})_{4-8}(\text{AlSiO}_4)_6\text{SO}_4$) and hauyne ($(\text{Na},\text{Ca})(\text{AlSiO}_4)_6(\text{SO}_4,\text{S})_{1-2}$) form a complete solid solution, but sodalite takes less than 10 weight percent of either into solid solution at 600°C and $P_{\text{H}_2\text{O}} = 1000$ bars. Potassium is recognized by Taylor (1967) as a major constituent of the hauyne-nosean series. From 0.1 to 5.44 percent K_2O has been reported in hauyne. In hauyne, calcium substitutes for sodium and enrichment in sulfate occurs. CaO and Na_2O are normally present in the ranges 0.2 to 10.2 and 10.39 and 23.90 percent, respectively. Some substitution of chloride and sulfide for sulfate is

observed. Lazurite contains sulfide and minor amounts of sulfate as interframework ions. Rogers (1938) suggested that the name lazurite be retained for the sulfide-rich end-member, $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_2$.

From analyses of fourteen noseans and hauynes, Taylor reports 0.19 to 2.60 percent Fe_2O_3 . If the ferric iron content is added to the aluminum content, then the Si:Al ratio is very near the ideal value of one. Si:Al ratios for sodalite group minerals are usually greater than unity. For noseans and hauynes, substitution of sulfide and chloride for sulfate occurs to a minor extent. In the fourteen samples, water content varied from 0.40 to 4.60 percent, being higher for the noseans. Nosean has fewer interframework anions than other sodalite minerals and can therefore accommodate more water. Up to 1 weight percent CO_2 has been identified in sodalite and hauyne.

OCCURRENCE

Sodalite group minerals occur in undersaturated plutonic, volcanic and metasomatized carbonate rocks. Sodalite is commonly found in nepheline syenites and associated rock types. Common associations are cancrinite (a mineral similar to sodalite), melanite (a garnet, $\text{Ca}_3(\text{Fe},\text{Ti})_2\text{Si}_{13}\text{O}_{12}$) and nepheline ($\text{NaAlSi}_3\text{O}_8$). Sodalite is also common in alkali pegmatites. In volcanic rock sodalite occurs with or in place of nepheline in phonolites, and with leucite (KAlSi_2O_6) in tephrites and phonolites. Sodalite occurs in some trachytes and in cavities of ejected pyroclastic material. It is also found in some metasomatized calcareous rocks which are in contact with alkaline igneous assemblages.

The nosean-hauyne series occurs chiefly in phonolites, related volcanic rocks, and commonly in pyroclastic material. Nosean also occurs in syenites, while hauyne has been found in basalts.

Lazurite ($(\text{Na},\text{Ca})_8(\text{Al},\text{Si})_{12}\text{O}_{24}(\text{S},\text{SO}_4)$) is the rarest and most poorly understood member of the sodalite group. It occurs in metasomatized calcareous rocks. Associated minerals include pyrite (FeS), calcite (CaCO_3), sodalite and rarely nosean-hauyne.

ALTERATION

Mechanisms for the alteration of sodalite group minerals have not been examined in detail, but many hydrothermal alteration products have been identified. Sodalite ($\text{Na}_8(\text{AlSiO}_4)_6\text{Cl}_2$) altering to other zeolites has been mentioned most frequently. Thomsonite ($\text{NaCa}_2((\text{Al},\text{Si})\text{O}_2)_{10}\cdot 6\text{H}_2\text{O}$) natrolite ($\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}$) and gismondine ($\text{Ca}(\text{AlSiO}_4)_2\cdot 4\text{H}_2\text{O}$) have been identified (Deer, et al., 1963; Thugutt, 1946; Winchell and Winchell, 1967). These authors also report kaolinite (a clay mineral), diaspore ($\text{AlO}(\text{OH})$), gibbsite ($\text{Al}(\text{OH})_3$) and muscovite (a mica) as alteration products. Gerasimovsky (1937) reported sodalite ($\text{Na}_8(\text{AlSiO}_4)_6(\text{Cl},\text{S})_2$), variety hackmanite, altering to ussingite (a Na-zeolite). Sodalite altering to cancrinite ($((\text{Na},\text{Ca},\text{K})_{6-8}(\text{AlSiO}_4)_6(\text{CO}_3,\text{SO}_4,\text{Cl})_{1-2})$) has been reported by Deer, et al., (1963), Peteghem and Burley (1962), Thugutt (1946) and Winchell and Winchell (1927). The later authors have shown that nosean and hauyne transform to cancrinite at about 480°C in the pressure range 1000 to 2000 bars $P_{\text{H}_2\text{O}}$. They suggest this transformation to explain the almost exclusive occurrence of nosean and hauyne in volcanic rocks, while cancrinite is the common sulfate bearing tectosilicate in plutonic rocks. Cancrinite has the same framework stoichiometry as sodalite.

SODALITE

Structure

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SPINEL GROUP: $(\text{Fe},\text{Ni})(\text{Fe},\text{Cr})_2\text{O}_4$

A spinel phase occurs in supercalcine. Natural spinels such as $(\text{Fe},\text{Ni})\text{Fe}_2\text{O}_4$ and FeCr_2O_4 are close compositional analogues for supercalcine spinel, $(\text{Fe},\text{Ni})(\text{Fe},\text{Cr})_2\text{O}_4$. Spinel occurs in a wide range of geologic environments. They are durable.

MINERAL DATA

Mineral data for selected spinel group minerals are as follows:

Formula:	Magnetite (Fe_3O_4)	Trevorite (NiFe_2O_4)
Crystal System:	Cubic	Cubic
Space Group:	Fd3m	Fd3m
Z:	8	8
Lattice Constant:	$a = 8.394 - 8.396 \text{ \AA}$	$a = 8.34 - 8.43 \text{ \AA}$
Mohs Hardness:	5 1/2 - 6 1/2	5+
Density (gm/cm^3):	4.9 - 5.2	5.165 (meas), 5.24 (calc)

Formula:	Chromite (FeCr_2O_4)
Crystal System:	Cubic
Space Group:	Fd3m
Z:	8
Lattice Constant:	$a = 8.344 - 8.378 \text{ \AA}$
Mohs Hardness:	5 1/2
Density (gm/cm^3):	4.5 - 4.9 (meas), 5.09 (calc)

STRUCTURE

The term spinel, as it is normally used refers to a mineral, MgAl_2O_4 . The supercalcine "spinel" phase would be a $(\text{Ni,Fe})\text{Fe}_2\text{O}_4$ spinel with uncertain amounts of Cr, Ti and Al.

Bragg (1915a) and Nishikawa (1915) first determined the structure of the spinel group to which chromite (FeCr_2O_4), magnetite (Fe_3O_4), and trevorite (NiFe_2O_4) belong.

The spinel group of AB_2O_4 minerals may be broken down into three series according to whether the dominant B^{+3} ion is Cr, Fe, or Al. The chromite, magnetite and spinel series have the general formulas ACr_2O_4 , AFe_2O_4 and AAl_2O_4 , respectively. The varieties of a particular series are determined by the dominant A^{+2} ion (Deer, Howie and Zussman, 1966).

The chromite (FeCr_2O_4) and spinel (MgAl_2O_4) series have the normal spinel structure while the magnetite series has the inverse spinel structure. Both normal and inverse spinels belong to space group $\text{Fd}\bar{3}\text{m}$ and have eight AB_2O_4 formulas per unit cell. Both structures have an approximate cubic close packed (ccp) arrangement of 32 oxide ions per unit cell, Figure 17. There are one octahedral and two tetrahedral interstitial voids per oxygen. One half of the octahedral and one eighth of the tetrahedral interstices are occupied by cations. In normal spinels, octahedral holes are occupied by B^{+3} cations and the tetrahedral holes are occupied by A^{+2} cations. The inverse structure occurs when A^{+2} ions have a stronger preference for octahedral coordination than B^{+3} ions. The result is that A^{+2} ions and one half of the B^{+3} ions occupy octahedral sites. Cation disordered spinels in which only a fraction of the A^{+2} ions are in tetrahedral coordination occur when A^{+2} and B^{+3} ions have similar preferences for tetrahedral and octahedral sites (Cotton and Wilkinson, 1972). All spinels have layers of oxygen ions which alternate with layers of cations perpendicular to the threefold axes. Cation layers in which all the cations are in B positions alternate with layers in which one third of the cations are in B positions and two thirds are in A

Figure 17: (A) The spinel structure and (B) an alternative representation of the spinel structure where the unit cell has been shifted by $a/2$ (Verwey and Heilmann, 1947)

positions. Each oxygen ion coordinates with one A ion and three B ions.

A class of tetragonal "spinel" including CuFe_2O_4 , MnMn_2O_4 , and ZnMn_2O_4 have a slightly elongated c-axis. McClure (1957) and others suggest that tetragonal "spinel" are the result of a Jahn-Teller distortion, a well documented phenomenon for Cu^{+2} and Mn^{+3} ions (Cotton and Wilkinson, 1972).

Attempts to predict which spinels will be inversed on the basis of ionic radii and lattice energy considerations have not been successful (McClure, 1957). With the exception of Al, most cations which occur in spinels are moderately sized, thus ionic radii are usually not a factor. Lattice energy calculations suggest that all $\text{A}^{+2}\text{B}^{+3}$ spinels should be normal (Verwey and Heilmann, 1947), which is incorrect. Spectroscopic data and CFT (crystal field theory) can be used to predict whether transition metal spinels are normal or inverted (McClure, 1957), Table 15. Such an approach is not applicable to spinels which contain Al (non-transition metal) or d^{10} or d^5 high spin ions.

By comparing the intensities of the 400 and 224 reflections for a spinel, one can infer whether it is normal or inverted (Greenwald, Pickart and Grannis, 1954), Figures 18a and 18 b. This method becomes increasingly sensitive as the difference in x-ray scattering power of A and B ions increases.

CHEMISTRY

Minerals with the spinel structure occur only rarely as pure or nearly pure end-members.

Chromites form a solid solution between FeCr_2O_4 and MgCr_2O_4 (Lindsley, 1976). Magnesiochromite is the varietal name given to those chromites which contain more Mg^{+2} than Fe^{+2} (Deer et al., 1962). Donath (1931) reported a zinc containing chromite from Norway and a chromite containing both zinc and lead has been found in Yugoslavia (Deleon, 1955). Aluminum and iron frequently substitute

Table 15: Theoretical and experimental cation distributions in $A^{+2}B_2^{+3}O_4$ spinels (After McClure, 1957).

A ^B	Al ⁺³		Ga ⁺³		Fe ⁺³		Cr ⁺³		Mn ⁺³		V ⁺³		Co ⁺³	
	Exp.	Th.	Exp.	Th.	Exp.	Th.	Exp.	Th.	Exp.	Th.	Exp.	Th.	Exp.	Th.
Mg ⁺²	.88 I	0	I	0	I	0	N	N	--	N	N	N	--	N
Zn ⁺²	N	0	N	0	N	0	N	N	N, T	N	N	N		
Cd ⁺²	N	0	N	0	N	0	N	N	--	N	--	N	--	N
Mn ⁺²	N	0	--	0	I	0	N	N		N	N	N	--	N
Fe ⁺²	N	I	--	I	I	I	N	N	--	N	N	I+N	--	N
Co ⁺²	N	I	--	I	I	I	N	N	--	N	--	I+N		
Ni ⁺²	3/4 I +1/4 N	I	I	I	I	I	N	N	--	I+N	--	I	--	I
Cu ⁺²	I	I	--	I	.86 I, I T		N	N	--	N	--	I	--	N

N = normal, I = inverse, T = tetragonal, 0 -- no prediction made by CFT

(a)

(b)

Figure 18: a) Calculated curves of the (400/224) intensity ratios for NiOAl_2O_3 as a function of the fraction of Ni^{++} in the A-sites (Greenwald Pickart and Grannis, 1954).
 b) Calculated curves of the (400/220) and (400/224) intensity ratios in NiOGa_2O_3 as a function of the fraction of Ni^{++} in the A-sites (Greenwald, Pickart and Grannis, 1954).

for Cr. An analysis of seven chromites indicated an Al content ranging from 10.2 - 22.93 weight percent and an Fe_2O_3 content ranging from 2.87 - 11.20 weight percent, Table 16. Lunar chromites can contain significant amounts of Fe_2TiO_4 but TiO_2 is a minor constituent (usually less than 1 weight percent) of terrestrial chromites. Inclusions in chromite include hematite (Fe_2O_3), magnetite (Fe_3O_4) as exsolution lamelle, and metamorphic silicate minerals (Deer *et al.*, 1962).

Katsura and Muan (1964) have studied the system $\text{FeO} - \text{Fe}_2\text{O}_3 - \text{Cr}_2\text{O}_3$ at 1300° and 1 atm total pressure, Figure 19. In regions deficient in FeO, a spinel phase and a $(\text{Fe,Cr})_2\text{O}_3$ phase are in equilibrium. In regions where FeO is present in excess, the spinel phase is found in equilibrium with Fe, wustite, or both Fe and wustite (Katsura and Muan, 1964).

Trevorite (NiFe_2O_4) and magnetite (Fe_3O_4) represent the end members of an isomorphous series. De Waal (1972) has divided the series on the basis of the number of Ni ions per 32 oxygen ions as follows:

- 0 - 2 Ni ions, magnetite
- 2 - 4 Ni ions, nickeloan magnetite
- 4 - 6 Ni ions, ferroan trevorite
- 6 - 8 Ni ions, trevorite.

Table 17 lists cell dimensions and densities for some compositions of the magnetite-trevorite solid solution series. Considerable amounts of Mg can substitute for Fe in magnetite, giving rise to the variety magnesioferrite. A solid solution series between magnetite and Fe_2TiO_4 (ulvospinel) also exists. Ulvospinel and ilmenite (FeTiO_3) sometimes occur as exsolution lamelle in magnetite (Vincent *et al.*, 1957). Magnetite forms a solid solution with FeAl_2O_4 (hercynite) above 858° , below that temperature a two phase region of exsolution forms (Deer, Howie and Zussman, 1966). Table 18 lists the elemental composition of a number of spinels in the magnetite series.

Table 16: Chemical Analyses of chromite (Deer et al., 1962). Values are given as weight percent.

	1.	2.	3.	4.	5.	6.	7.
SiO ₂	0.24	1.80	0.12	0.36	---	0.08	0.22
TiO ₂	0.17	0.10	0.14	---	0.69	0.56	0.43
Al ₂ O ₃	14.03	13.50	10.23	13.67	13.36	22.93	16.90
Cr ₂ O ₃	55.51	47.25	59.40	51.54	52.77	34.81	47.82
Fe ₂ O ₃	3.79	11.20	3.30	6.01	2.87	10.83	5.30
FeO	11.35	12.45	14.09	16.09	19.20	21.24	16.45
MnO	0.14	0.01	0.14	0.32	0.20	0.22	0.16
MgO	14.83	13.65	12.62	11.98	10.31	9.74	12.11
CaO	0.11	---	0.14	trace	0.28	0.06	0.04
H ₂ O	0.09	---	---	---	---	---	0.26
Total	100.25	99.96	100.23	99.97	99.68	100.47	99.73

Figure 19: The system $\text{FeO}-\text{Fe}_2\text{O}_3-\text{Cr}_2\text{O}_3$ at 1300°C and 1 atm total pressure (Katsura and Muan 1964). FO_2 ranged from 0.21 to $10^{-10.8}$ atm. SP = chromite - magnetite solid solution, $\text{R}_2\text{O}_3 = (\text{Cr, Fe})_2\text{O}_3$ solid solution, Wüs = wustite, Mt = magnetite (Lindsley, 1976).

Table 17: Unit Cell Dimensions of Trevorite and Magnetite

	a_0 (Å)	Density (gm/cm ³)	Ni ions/ unit cell	Author
Trevorite	8.43	5.26		Deer <u>et al.</u> , 1962
Trevorite	8.339 (.001)	5.332 (.015) obs. 5.349 calc.	7.703	De Waal, 1972
Ferroan trevorite	8.367 (.003)	5.212 (.007) obs. 5.227 calc.	4.156	De Waal, 1972
Trevorite, synthetic	8.339	5.369	8.0	JCPDS file
Magnetite	8.396	5.20	--	Deer et al., 1962
Magnetite	8.396	5.196 calc.	0.0	De Waal, 1972

Table 18: Chemical analyses of trevorite and some other spinels of the magnetite series. Values are given as weight percent.

	1.	2.	3.	4.	5.	6.
SiO ₂	0.36	0.66	1.40	0.03	0.10	1.15
Cr ₂ O ₃	0.37	---	---	---	0.07	---
Al ₂ O ₃	0.22	0.03	---	0.19	1.39	0.04
Fe ₂ O ₃	66.33	68.51	66.24	68.95	28.37	89.15
MnO	0.04	0.00	---	---	0.33	---
MgO	0.03	0.07	0.24	---	2.29	trace
CoO	0.43	0.32	---	---	---	---
NiO	30.42	16.75	29.71	---	---	---
CaO	0.65	0.04	---	0.02	0.06	trace
TiO ₂	---	---	---	---	19.42	1.37
FeO	---	13.00	1.96	30.82	46.06	8.67
H ₂ O	n.d.	n.d.	0.36	0.04	---	---

1. De Waal (1972)

2. De Waal (1969)

3 - 4. Deer et al. (1962)

5 - 6. Deer et al. (1966)

OCCURRENCE

Chromite occurs in olivine-rich (commonly serpentized) ultrabasic (i.e., rock containing less than 45 percent SiO_2) igneous rocks. It is frequently associated with pyroxene (Ca,Mg,Fe,...SiO_3), talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$), magnetite, pyrrhotite ($\text{Fe}_{(1-x)}\text{S}$) and uvarovite ($\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3$). It is ubiquitous in most meteorites. An early mineral in the paragenesis of minerals from a melt, it forms cummulative layers, although much of this may be chromium spinel, $(\text{Mg, Fe})(\text{Al, Cr})_2\text{O}_4$, rather than chromite (Deer *et al.*, 1962). Its stability allows detrital stream and beach accumulations. It is a constituent in fossil placers.

Trevorite is a rare mineral which occurs in nickel rich ores near the Scotio Talc Mine, Barberton, South Africa. DeWaal (1969, 1970, 1972) reports that ferroan trevorite occurs in a nickel-rich talc as clusters of minute grains. Associated with it are violarite $(\text{Ni,Fe})_2\text{S}_3$, millerite (NiS) as minute inclusions, nickel rich chlorite $(\text{Mg,Al,Fe,Ni})_{12}(\text{Si,Al})_8\text{O}_{20}(\text{OH})_{16}$, reevesite and opal as secondary alteration products of the ore, and a soft, green unidentified silicate. DeWaal (1972) also reports a nickel-rich trevorite from the same locality which is associated with nickel-rich varieties of olivine (Mg_2SiO_4), serpentine ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$) and chlorite.

Magnetite is a common mineral in igneous and metamorphic rocks. Usually it occurs as an accessory mineral in igneous rocks but can be concentrated by crystal settling or some other process to form magnetite bands. In basic igneous rocks, magnetites often contain appreciable amounts of TiO_2 . Skarn deposits sometimes contain magnetite as a replacement (i.e., metasomatic) mineral. In skarn deposits it is associated with Pb, Zn and Cu oxides or sulfides as well as iron-calcium rich garnets (i.e., andradite, $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$) and pyroxene (var. hedenbergite, $\text{Ca}(\text{Mg,Fe})\text{Si}_2\text{O}_6$). In thermally metamorphosed sediments magnetite results from reductions of hydrated ferric hydroxide ($\text{Fe}(\text{OH})_3 \cdot n\text{H}_2\text{O}$). It is sufficiently resistant to become concentrated as magnetite sands by the action of water.

ALTERATION

Alteration products of chromite include magnetite (Horninger, 1941), mixtures of chrome spinels and magnetite (Den Tex, 1955), chrome spinels and maghemite (Fe_2O_3) (Deer *et al.*, 1962), iron rich chromite or magnetite with martite (Fe_2O_3) (Baker, 1956, 1962), the chromian equivalent of martite ($(\text{Cr,Fe})_2\text{O}_3$) (Mukherjee, 1966), mixtures of chrome and iron rich spinels with hematite (Fe_2O_3) or eskolaite (Cr_2O_3) (Golding and Bayliss, 1968) magnetite-chromite (Figure 20) (Spangenberg, 1943; Beeson and Jackson, 1969; Ulmer, 1974) magnetite-chromite or magnetite (Weiser, 1967), magnetite-chromite or chrome bearing magnetite (Onyeagocha, 1974) and colloidal alteration products (Heistleitner, 1952). Most workers show the altered rinds are enriched in chromium, total iron and depleted magnesium and aluminum, Table 19. Golding and Bayliss (1968) attribute this trend to the greater stability of the Fe^{+3} and Cr^{+3} ions in the chromite structure. A vacancy left by an Fe^{+2} ion would be filled by an Fe^{+3} ion in a tetrahedral site and displace aluminum or magnesium.

Horninger (1941) suggests the alteration takes place by exchange of material with the country rock. Either magnesium and aluminum are removed from the chromite or iron is added.

Spangenberg (1943) believes chromite alteration is related to serpentization and chloritization of the country rock. Serpentization is the process of alteration of ultrabasic minerals such as pyroxene ($(\text{Mg,Fe})\text{SiO}_3$) to serpentine ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$). Chloritization is the process of hydrothermal alteration of rocks to chlorite ($(\text{Mg,Al,Fe})_{12}(\text{Si,Al})_8\text{O}_{20}(\text{OH})_{16}$). Beeson and Jackson (1969) explained the rinds by diffusion of Mg and Al out of the chromite during serpentization producing magnetite-chromite associated with a chloritized silicate. Kern (1968) reports chromite alteration is related to serpentization that may have been caused by late pneumatolytic hydrothermal solutions.

Chromite associated with serpentinites from the Pennsylvania

Figure 20: Typical quantitative electron microprobe analyses of a disseminated chromite grain. Data are given as weight percent (Ulmer, 1974).

Table 19: Chromite Alteration Pattern (Onyeagocha, 1974).

Chromite core Enriched in:	Ferrite- chromite rind enriched in:	Author
Al, Mg	Fe, Cr	Weiser, 1967, case 1
Al, Mg, Cr	Fe	Weiser, 1967, case 2
Al, Mg, Cr	Fe	Beeson and Jackson, 1969.
Al,	Fe	White, 1966
Cr	Fe	Muir and Tilley, 1964
Cr, Al, Mg, Zn	Fe, Ti, Ni	Frisch, 1971
Al, Mg	Fe, Cr, Ni, Mn, Co, Ti, Zn, V	Onyeagocha, 1974
Cr, Al, Mg	Fe, Co, Zn, Ni	Onyeagocha, 1974

State Line District have been described by Ulmer (1974). He suggested that mobilization and reprecipitation of chromite by deuteritic solutions is a possible mechanism for magnetite-chromite formation. Alternatively, a precipitation overgrowth of magnetite-chromite may be possible (Ulmer, 1974).

Onyeagocha (1974) studied two types of chromite alteration from the Twin Sisters Dunite, Washington: magnetite-chromite and magnetite. For these chromites he determined the alteration occurs above 570°C, the upper stability limit of serpentine at 10 kbar PH_2O and below 800°C, the upper stability limit of chlorite.

At 25°C and a pH of 5.6, chromite solubility is 5-10 ppm (Ulmer, 1974). According to Hem (1977), the presence of ferrous iron (Fe^{+2}) decreases the solubility of chromite. At pH 6 and a ferrous iron concentration of 10^{-10}M , the solubility of chromite is 10^{-10} moles Cr/liter (i.e. 5×10^{-6} ppm), Figure 21a. Trevorite as well as Cu and Zn-ferrite solubilities in the presence of ferric hydroxide have also been considered by Hem (1977). He reports that solubilities of these species are also quite low, Figure 21b.

The solubility of iron as a function of Eh-pH and pH have been studied by Garrels and Christ (1965), and Stumm and Lee (1960) respectively. In oxygenated natural waters, solubility is low at pH 7 (Garrels and Christ, 1964), but may reach 500 ppm in subsurface waters (White et al., 1963).

At surface conditions magnetite is oxidized to maghemite ($\gamma\text{-Fe}_2\text{O}_3$, defect spinel structure). Northrop (1959) indicates that maghemite forms as an alteration rind on magnetite. Metastable maghemite then transforms to hematite (Fe_2O_3) and ultimately to goethite (FeOOH) (Northrop, 1959). Limonite, an amorphous and hydrous form of hematite is an oxidation product of magnetite. It may be deposited from natural water at low temperatures and pressures in marshy areas, or it may be formed as a replacement product (Ford, 1949). Eh-pH and Eh- pS^{-2} diagrams indicate that magnetite stability is limited to reducing environments with high pH and PS^{-2} values, Figures 22a and 22b (Wedepohl, 1970; Berner, 1964).

(a)

(b)

Figure 21: a) Equilibrium solubility of chromite (FeCr_2O_4) at 25°C (Hem, 1977).

b) Equilibrium solubilities of three ferrites in the presence of ferric hydroxide and a fixed total bicarbonate activity of $10^{-3.00}\text{M}$ at 25°C and 1 atm. Dissolved metal concentrations include free metal ions and hydroxide and carbonate complexes ($10^{-7.00}\text{moles/l} = 6.4\text{ ug Ni/l}$ or 6.5 ug Ni/l (Hem 1977)).

(a)

(b)

Figure 22: a) An Eh-pH diagram showing the stability fields of hematite, siderite, pyrite, magnetite and pyrrhotite in water. 1 atm total pressure, $T = 25^{\circ}\text{C}$, $s = 10^{-1.5}$, $\text{CO}_2 = 10^{-2.5}$ (ΣS and ΣCO_2 as in seawater) (Wedephol 1970). b) An Eh- $p\text{S}^{2-}$ diagram showing the stability fields of hematite, siderite, pyrite, magnetite, and pyrrhotite in anaerobic marine sediments. Total pressure of 1 atm, $P_{\text{CO}_2} = 10^{-2.5}$, $\text{pH} = 7.5$, $T = 25^{\circ}\text{C}$ (Wedephol, 1970; after Berner, 1964).

RADIATION DAMAGE

Damage in chromite caused by surrounding radioactive minerals has been described by Liebenberg (1955) and Mihalik and Saager (1968). In the Witwatersrand chromites, studied by Mihalik and Saager (1968), chromites abutting uraninite or other radioactive minerals showed a widening of the alteration rind. They suggest lattice destruction caused by radioactive minerals, aided the leaching of MgO from the lattice and its replacement by FeO. Although Cr and Al content did not change in this case, he reports a decrease in Mg and Al. An increase in Fe and possible increase of Cr has been found in other cases. Widening of the alteration zone of chromites associated with radioactive minerals has also been reported by Ramdohr (1950)

SPINEL GROUP

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APATITE GROUP: $A_5(XO_4)_3(O,OH,X)$

Britholite, $(Ca,Ce)_5(SiO_4,PO_4)_3(OH,F)$ is a close compositional analogue to the supercalcine apatite phase, $CaRE_4(SiO_4)_6O$. Britholite occurs in syenitic and granites. It is subject to radiation damage (metamictization) and oxidation of Ce^{+3} , but it is a durable mineral.

MINERAL DATA

Mineral data for britholite are as follows:

Formula: $(\text{Ca,Ce})_5(\text{SiO}_4, \text{PO}_4)_3(\text{OH,F})$

Crystal System:	Hexagonal
Space Group:	$P6_3/m$
Z:	2
Unit Cell Parameters:	$a = 9.61\text{--}9.63$ $c = 7.02\text{--}7.03\text{\AA}$
Mohs Hardness:	5
Density (gm/cm^3):	3.86–4.69 (Meas.) 3.95–4.65 (Calc.)

STRUCTURE

The structure of apatite has been determined by Haray-Szabo (1930), Hendricks et al., (1932) and Beevers and McIntyre (1946). Most members of the apatite group are hexagonal and have $P6_3/m$ space group symmetry. In the fluorapatite structure, there are two $Ca_4(PO_4)_3F$ formulas per unit cell and two distinct types of Ca ions. The first type lies on the plane $z = .25$ along with the fluorine ions and phosphorous ions. These Ca and P ions form hexagonal prisms about 0,0,z, enclosing the F ions. Each F ion coordinates with three Ca ions of the first type, while they each coordinate with five oxygens. The second type of Ca ion lies on the plane $z = 0$ and coordinates with six oxygens Figure 23.

CHEMISTRY

Extensive amounts of substitution are observed in the apatite structure, $Ca_5(PO_4)_3(F,OH,O)$. Ca can be replaced by Na, K, Mn, Mg, Pb, Sr, Ce and other rare earth elements, U and Th. The phosphate groups can be replaced by sulfate, silicate, carbonate, arsenate or vanadate groups. Fluoride ions may be replaced by oxide, hydroxide, or chloride ions. The substitution patterns in apatite minerals are often complex.

Cockbain (1968) has broken the apatite family, $A_5(XO_4)_3Z$ into three groups according to the A:X radius ratio, Table 20. Vanadinite-svabites have a radius ratio of less than 2.5-2.6, apatite-mimetites have a radius ratio of 2.6-3.23 while pyromorphites have a radius ratio which is larger than 3.3. In general there is extensive solution within these groups but limited or no solid solution among them. Most of the silicate apatites belong to the apatite-mimetite group.

Britholite $(Ca,REE,Th)_5((Si,Al,P)O_4)_3(OH,F)$ is a close natural analogue to the REE-silicate apatite phase in supercalcine. Britholite can contain up to 56 wt% REE, including 19 wt% Y and the heavy REE.

Table 20: A Classification of Natural and Synthetic Apatites into Groups According to their Radius Ratios (Cockbain, 1968)

Group I apatites The vanadinite-syabites		Group II apatites The apatite-mimetites	
Composition	A-X ratio	Composition	A-X ratio
$\text{La}_8(\text{GeO}_4)_6$	1.89	$\text{Ca}_6\text{Nd}_4(\text{SiO}_4)_6$	2.62
$\text{Ca}_{10}(\text{CrO}_4)_6(\text{OH})_2$	1.94	$\text{Ca}_4\text{Nd}_6(\text{SiO}_4)_6(\text{OH})_2$	2.65
$\text{Pb}_8\text{Na}(\text{VO}_4)_6$	2.13	$\text{Ca}_8\text{Ce}_2\text{La}_2(\text{SiO}_4)_6$	2.68
$\text{Ca}_4\text{Ce}_2(\text{GeO}_4)_6\text{Cl}_2$	2.16	$\text{Ca}_8\text{Ce}_2(\text{GeO}_4)_2(\text{PO}_4)_4$	2.68
$\text{Ca}_6\text{La}_4(\text{GeO}_4)_6$	2.18	$\text{Pb}_8\text{Na}_2(\text{AsO}_4)_6$	2.71
$\text{Ca}_4\text{La}_3(\text{GeO}_4)_6(\text{OH})_2$	2.20	$\text{Pb}_{10}(\text{GeO}_4)_2(\text{AsO}_4)_4$	2.71
$\text{Pb}_{10}(\text{VO}_4)_6(\text{F}, \text{Cl}, \text{Br}, \text{I})_2$	2.21	$\text{Ca}_{10}\text{La}_5\text{Ce}_5(\text{SiO}_4)_{12}(\text{OH})_2$	2.71
$\text{Pb}_8\text{Ti}_2(\text{VO}_4)_6$	2.22(2.13-2.32)	$\text{Ca}_6\text{La}_4(\text{SiO}_4)_6$	2.72
$\text{Ca}_4\text{La}_6(\text{GeO}_4)_6(\text{OH})_2$	2.24	$\text{Ca}_4\text{La}_3\text{Ce}_3(\text{SiO}_4)_6(\text{OH})_2$	2.74
$\text{Pb}_8\text{K}_2(\text{VO}_4)_6$	2.26	$\text{Ca}_5\text{La}_5(\text{SiO}_4)_6\text{OH}$	2.76
$\text{Sr}_4\text{Dd}_6(\text{SiO}_4)_6(\text{OH})_2^*$	2.26	$\text{Ca}_4\text{La}_6(\text{SiO}_4)_6(\text{OH})_2$	2.80
$\text{Pb}_{10}(\text{GeO}_4)_2(\text{VO}_4)_4$	2.30	$\text{Ca}_4\text{La}_6(\text{SiO}_4)_6\text{F}_2$	2.80
$\text{Sr}_4\text{La}_6(\text{GeO}_4)_6(\text{OH})_2$	2.34'	$\text{Pb}_8\text{KNa}(\text{AsO}_4)_6$	2.80
$\text{Ca}_{10}(\text{AsO}_4)_6(\text{F}, \text{Cl})_2$	2.34	$\text{Pb}_{10}(\text{AsO}_4)_6(\text{F}, \text{Cl}, \text{Br}, \text{I})_2$	2.82
$\text{Ca}_4\text{Ce}_6(\text{GeO}_4)_4(\text{SiO}_4)_2\text{Cl}_2$	2.34	$\text{Pb}_8\text{Ti}_2(\text{AsO}_4)_6$	2.82(2.70 - 2.95)
$\text{La}_8(\text{SiO}_4)_6$	2.36	$\text{Ti}_2\text{La}_8(\text{SiO}_4)_6(\text{OH})_2$	2.85
$\text{Ca}_6\text{Ce}_4(\text{GeO}_4)_4(\text{PO}_4)_2\text{Cl}_2$	2.41	$\text{Ba}_{10}(\text{MnO}_4)_6(\text{OH})_2$	2.86
$\text{Ca}_4\text{Y}_6(\text{SiO}_4)_6(\text{OH})_2$	2.45	$\text{Ba}_{10}(\text{CrO}_4)_6(\text{OH})_2$	2.86
$\text{Ba}_2\text{La}_8(\text{GeO}_4)_6\text{O}_2$	2.45	$\text{Pb}_8\text{K}_2(\text{AsO}_4)_6$	2.89
$\text{Ba}_3\text{La}_7(\text{GeO}_4)_6\text{O}_{1.5}$	2.49	$\text{Pb}_{10}(\text{SiO}_4)_2(\text{AsO}_4)_4$	2.91
$\text{Ca}_4\text{Ce}_6(\text{GeO}_4)_2(\text{SiO}_4)_4\text{Cl}_2$	2.49	$\text{Sr}_4\text{La}_6(\text{SiO}_4)_6(\text{OH})_2$	2.93
$\text{Ba}_{10}(\text{VO}_4)_6(\text{OH})_2$	2.50	$\text{Pb}_8\text{Rb}_2(\text{AsO}_4)_6$	2.96
$\text{Pb}_{10}(\text{SiO}_4)_2(\text{VO}_4)_4$	2.51	$\text{Pb}_{10}(\text{SiO}_4)_2(\text{VO}_4)_2(\text{PO}_4)_2$	3.02
$\text{Sr}_{10}(\text{MnO}_4)_6(\text{OH})_2$ (?)	2.52	$\text{Ca}_9\text{Mg}(\text{PO}_4)_6\text{Cl}_2$	3.02
		$\text{Ca}_9\text{Ni}(\text{PO}_4)_6\text{O}$	3.03
		$\text{Ca}_{10}(\text{SiO}_4)_3(\text{SO}_4)_3(\text{OH})_3$	3.03
		$\text{Pb}_{10}(\text{SiO}_4)(\text{GeO}_4)(\text{PO}_4)_2(\text{AsO}_4)_2$	3.05
		$\text{Ca}_5\text{Cd}_5(\text{PO}_4)_6\text{F}_2$	3.09
		$\text{Ba}_3\text{La}_7(\text{SiO}_4)_6(\text{OH})_2$	3.11
		$\text{Ca}_9\text{Cd}(\text{PO}_4)_6\text{F}_2$	3.11
		$\text{Ca}_{10}(\text{PO}_4)_6(\text{F}, \text{Cl}, \text{Br}, \text{OH})_2$	3.12
		$\text{Pb}_8\text{Bi}_2(\text{SiO}_4)_4(\text{PO}_4)_2$	3.16
		$\text{Ca}_9\text{Sr}(\text{PO}_4)_6\text{O}$	3.16
		$\text{Ca}_9\text{Pb}(\text{PO}_4)_6(\text{O}, \text{Cl}_2)$	3.18
		$\text{Ca}_9\text{Ba}(\text{PO}_4)_6(\text{O}, \text{Cl}_2)$	3.23

* Dd_2O_2 = Didymium oxide.

Table 20: A Classification of Natural and Synthetic Apatites into Groups According to their Radius Ratios (Cockbain, 1968) (continued)

Group III Apatites, The Pyromorphites	
Composition	A-X ratio
$\text{Pb}_{10}(\text{GeO}_4)_2(\text{PO}_4)_4$	3.33
$\text{Pb}_{10}(\text{SiO}_4)(\text{GeO}_4)(\text{PO}_4)_4$	3.44
$\text{Pb}_{10}(\text{PO}_4)_4(\text{SiO}_4)_2$	3.49
$\text{Pb}_8\text{Na}_2(\text{SO}_4)_2(\text{PO}_4)_2(\text{SiO}_4)_2$	3.50
$\text{Sr}_{10}(\text{PO}_4)_6(\text{OH},\text{F})_2$	3.51
$\text{Ca}_4\text{Na}_6(\text{SO}_4)_6\text{F}_2$	3.52
$\text{Pb}_9\text{Na}(\text{PO}_4)_5\text{SiO}_4$	3.59
$\text{Pb}_8\text{Na}_2(\text{PO}_4)_6$	3.62
$\text{Pb}_8\text{KNa}(\text{PO}_4)_6$	3.73
$\text{Pb}_{10}(\text{PO}_4)_6(\text{F},\text{Cl},\text{Br},\text{OH})_2$	3.76
$\text{Pb}_8\text{Tl}_2(\text{PO}_4)_6$	3.80
$\text{Pb}_8\text{K}_2(\text{PO}_4)_6$	3.85
$\text{Pb}_8\text{Rb}_2(\text{PO}_4)_6$	3.94
$\text{Pb}_8\text{Cs}_2(\text{PO}_4)_6$	4.06
$\text{Ba}_{10}(\text{PO}_4)_6(\text{F},\text{OH})_2$	4.24
$\text{Pb}_{10}(\text{SiO}_4)_2(\text{BO}_3)_4$	4.43

Figure 23: A representation of the fluorapatite structure. The lower half of the unit cell is included along with a representation of the space group $P6_3/m$ (modified from Deer et al., 1962).

Britholite commonly contains a few wt% ThO_2 and can contain at least 19 wt% ThO_2 . Major amounts of P or Al can substitute for Si. CaO is present in amounts of 10–17 wt% but SrO rarely exceeds 1 wt%. The compositions of britholites and related apatite group minerals are included in Table 21.

OCCURRENCE

Apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH},\text{F})$) is a common accessory mineral in igneous rocks, pegmatites, metamorphic rocks and sedimentary rocks both as a detrital mineral and as a primary deposit. It also occurs in hydrothermal veins and cavities and in carbonatites (Deer et al., 1962). In general chlorapatite is more common in basic igneous rocks, fluorapatite in granite rocks and Sr-, RE-, Th- and silicate-apatites occur in nepheline syenite pegmatites (Heinrich, 1965).

Britholite occurs in nepheline syenites, alkali syenites, granites and pegmatites. Associated minerals include quartz, feldspars ($(\text{Na},\text{K},\text{Ca})\text{AlSi}_2(\text{Al},\text{Si})\text{O}_8$), nepheline (NaAlSiO_4), amphiboles, pyroxenes ($(\text{Ca},\text{Mg},\text{Fe})\text{SiO}_3$), natrolite (a zeolite, $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$), fluorite (CaF_2) and niobate minerals. Descriptions of britholite occurrences indicate that it is a late stage mineral, often of metasomatic origin (i.e., formed by replacement of older rock under hydrothermal conditions) (Leventov, 1964; Glushchenko and Li, 1966; Andreev, et al., 1969; and York, et al., 1961).

ALTERATION

Although the literature on weathered phosphate deposits is extensive (Smith and Whitlatch, 1940; Hutchinson, 1950; Malde, 1959; White and Warin, 1964; Altschuler, 1973; Deans, 1966), specific information on alteration of silicate apatites is meager.

Britholite is subject to oxidation by supergene conditions (ground waters which have been near the surface) and surface weathering. Under these conditions, cerianite ($(\text{Ce},\text{RE})\text{O}_2$) appears as

Table 21: Chemical Compositions and Densities of Some Silicate-, Rare Earth- and Strontium-Containing Apatites

Components	Britholite			Alumobritholite		Fynchenite	Yttrobritholite	Belovite	Lessignite	Beckelite
	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
Ce ₂ O ₃	19.04	22.48	} 54.47	} 27.58	} 56.96	12.98	4.47	} 24.00	22.48	28.10
La ₂ O ₃	18.04	36.01				20.07	5.76		36.65	31.60
Y ₂ O ₃	19.36	3.42				0.66	46.91		3.42	2.86
ThO ₂	0.32	0.64	4.13	4.76	-	19.64	0.51	-	-	-
UO ₂	-	-	-	0.63	-	-	-	-	-	-
P ₂ O ₅	2.56	1.13	3.66	3.96	3.84	6.32	1.73	28.88	1.12	-
Nb ₂ O ₅	0.41	-	0.05	-	-	-	-	-	-	-
ZrO ₂	-	-	0.02	0.98	-	-	-	-	-	-
SiO ₂	17.88	19.85	19.50	21.93	17.28	13.76	22.70	0.20	19.85	17.13
CO ₂	2.34	0.35	-	-	-	2.62	0.10	-	0.35	-
Fe ₂ O ₃	-	0.65	0.88	5.42	2.41	-	0.79	0.60	0.65	-
Al ₂ O ₃	0.49	0.26	0.17	14.91	-	-	0.75	-	0.26	0.30
CaO	12.64	11.71	13.31	17.34	11.51	10.43	9.58	5.23	11.71	15.46
SrO	0.07	-	0.69	-	-	-	-	33.60	-	-
MnO	0.62	0.88	0.08	-	-	-	3.67	-	0.88	0.07
MgO	0.11	0.17	-	-	-	-	0.10	0.16	0.17	-
FeO	-	-	-	0.32	-	-	1.44	-	-	-
Na ₂ O	-	0.08	0.14	0.30	1.50	-	-	3.60	0.08	0.78
K ₂ O	-	-	-	-	-	-	-	-	-	0.39
H ₂ O	4.86	1.94	1.60	0.70	6.40	10.33	0.83	0.89	1.94	0.99
F	2.38	0.54	2.61	1.66	-	-	0.50	-	0.54	-
TiO ₂	-	-	-	-	-	-	-	-	-	-
PbO	-	-	-	-	-	-	-	-	-	-
O = F ₂	1.00	0.23	1.05	0.69	-	-	0.21	-	-	-
Total	100.12	99.88	100.26	99.80	99.90	-	99.63	99.44	100.11	100.18
Density	4.08	4.694	4.519	3.95	4.062	3.327	-	-	-	-
1 - 8. Vlasov (1964)			9 - 10. Gay (1957)							

an alteration rind. Britholite is frequently hydrated, probably as a result of metamictization (radiation damage). Rare earth-carbonates, -phosphates and silicophosphates have been sited as alteration products of britholite (Vlasov, 1964; Glushchenko and Li, 1966; Kudrina, et al., 1961).

RADIATION DAMAGE

Thorian varieties of britholite with as little as 0.80 weight percent ThO_2 may show radiation damage effects. (Shlyukova, et al., 1965). Completely metamict varieties of britholite with 11 wt% ThO_2 are known. Crystalline structure is restored when metamict britholite is annealed at 900°C (Glushchenko and Li, 1966; Andreev, et al., 1969).

APATITE

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MONAZITE: (Ce,La,Th)PO₄

Monazite and huttonite (ThSiO₄) are analogues for the supercalcine monazite phase (Ce,La,U)PO₄. The mineral analogues are resistant to radiation damage and chemical alteration, although oxidation of Ce⁺³ may occur. Monazite occurs in a wide variety of primary and secondary environments.

MINERAL DATA

Mineral data for monazite and huttonite are as follows:

Formula:	Monazite ((Ce,La,Th)PO ₄)	Huttonite (ThSiO ₄)
Crystal System:	Monoclinic	Monoclinic
Space Group:	P2 ₁ /n	P2 ₁ /n
Z:	4	4
Lattice Constants:	a = 6.76 - 6.89 b = 6.99 - 7.05 c = 6.42 - 6.48 Å β = 103°10' - 30'	a = 6.78 - 6.80 b = 6.96 - 6.97 c = 6.50 - 6.54 Å β = 104°55'
Mohs Hardness:	5 - 5 1/2	Not determined
Density (gm/cm ³):	4.6 - 5.4	7.1 (Meas), 7.18 (Calc)

STRUCTURE

Monazite $(\text{Ce,L a})\text{PO}_4$, cheralite $(\text{Ce,L a,Th,C a,U})(\text{P,S i})\text{O}_4$ and huttonite (ThSiO_4) are isomorphous with $\text{P}2_1/\text{n}$ (i.e. $\text{P}2_1/\text{c}$ with a nonstandard choice of a_0 and c_0) space group symmetry. Each has four ABO_4 formulas per unit cell.

The huttonite structure is composed of a three dimensional network of edge-sharing ThO_9 polyhedra which are interconnected by SiO_4 tetrahedra, Figure 24. Each thorium atom coordinates to four axial and five equatorial oxygen atoms. The equatorial oxygen atoms are shared corners between ThO_9 and SiO_4 polyhedra while axial oxygen atoms compose shared edges. Th-O distances range from 2.40 - 2.81 Å. Three unique oxygen atoms are coordinated to one Si and two Th atoms, while the fourth is coordinated to an additional Th atom, Figure 25. ThO_9 and SiO_4 polyhedra form infinite nearly linear edge-sharing chains that are parallel to the c-axis (Taylor and Ewing, 1978).

Major amounts of isomorphous substitution with no major structural changes are observed for the huttonite-cheralite-monazite series (Bowie and Horne, 1953; Finney and Rao, 1967). Cheralite has Ce^{+3} , La^{+3} , Th^{+4} , U^{+4} , and Ca^{+2} as major cationic components. Substitution of the Ce-La earths by Th and U is usually compensated for by additional substitution of Ce-La by Ca^{+2} though replacement of P^{+5} by Si^{+4} may also occur. When the substitution by Th is compensated by the sole replacement of P^{+5} by Si^{+4} , huttonite is the resulting end-member. Shrinkage of the unit cell volume accompanies the substitution of Ce-La by Ca and Th (monazite cheralite), Table 22, (Bowie and Horne, 1953). Density and refractive index, n_y , increase from monazite to huttonite (Vlasov, 1964).

Low temperature and low density polymorphs of CePO_4 , LaPO_4 , and DyPO_4 have been prepared by precipitation from aqueous solution and by low temperature hydrothermal synthesis (Carron, et al., 1958). The structures are thought to have $\text{C}6_22$ (= $\text{P}6_222$) space group symmetry (Mooney, 1948). Their structures appear to be similar to the

Figure 24: A perspective polyhedral representation of huttonite.
Taylor and Ewing (1978).

Figure 25: (a) The coordination polyhedron of Th and (b) the c-axis chains in huttonite (Taylor and Ewing, 1978).

Table 22: Unit Cell Dimensions of Monazite and Some Isomorphous Materials with Monazite and Zircon

Composition	a (Å)	b (Å)	c (Å)	β	Author
Monazite (Th-bearing)	6.782	6.993	6.445	$103^{\circ}38'$	Gliszczynski, 1939
$\text{La}_4\text{Ce}_4\text{Y}(\text{PO}_4)_9$ (Th-free)	6.76	7.00	6.42	$103^{\circ}10'$	Parrish, 1939
LaPO_4	6.89	7.05	6.48	$103^{\circ}34'$	Mooney, 1948
CePO_4	6.76	7.00	6.44	$103^{\circ}38'$	Mooney, 1948
PrPO_4	6.75	6.94	6.40	$103^{\circ}21'$	Mooney, 1948
NdPO_4	6.71	6.92	6.36	$103^{\circ}28'$	Mooney, 1948
BiPO_4	6.78	6.99	6.45	104°	Zemann, 1949
Monazite, Tranvacore	6.79	7.04	6.47	$104^{\circ}4'$	Bowie and Horne, 1953
Monazite, Tranvacore	6.77	7.04	6.46	104°	Ghouse, 1965
Cheralite	6.717	6.920	6.434	$103^{\circ}30'$	Finney and Rao, 1967
Cheralite, Tranvacore	6.74	7.00	6.43	$104^{\circ}06'$	Bowie and Horne, 1953
Huttonite	6.80	6.96	6.54	$104^{\circ}55'$	Pabst, 1951
Huttonite, Synthetic	6.784 (2)	6.974 (3)	6.500 (3)	$104^{\circ}55(2)'$	Taylor and Ewing, 1978
$\text{CaTh}(\text{PO}_4)_2$	6.69	6.93	6.38	$102^{\circ}27'$	Gliszczynski, 1939

Table 22: Unit Cell Dimensions of Monazite and Some Isomorphous Materials with Monazite and Zircon (Continued).

Composition	a (Å)	c (Å)	Author
Zircon, ZrSiO_4	6.60	5.88	Wyckoff and Hendricks, 1927
Thorite, Synthetic	7.1328 (2)	6.3188 (2)	Taylor and Ewing, 1978
Thorite, ThSiO_4	6.315	5.667	Boldyrev, <u>et al.</u> , 1938
YVO_4	7.126	6.197	Broch, 1933

tetragonal zircon-thorite structure in the respect that there are chains of alternating phosphate and eight-coordinated Ce atoms parallel to the c-axis. Also, common to both structures are open channels parallel to the c-axis which may contain absorbed water. When dried at moderate temperatures these phosphates slowly convert to the monoclinic form (Mooney, 1948). The phosphates of Y, Tb, Dy, Ho, Er, Tm, and Yb have the tetragonal zircon-thorite structure (Feigelson, 1964). The structure of zircon has been described in detail by Robinson (1971). Thorite is the low temperature and low pressure polymorph of ThSiO_4 (Mumpton and Roy, 1961).

CHEMISTRY

Monazite is a thorium bearing phosphate of the rare earth elements La, Ce, Pr, Nd, Pm, Sm and Eu. The remaining rare earth elements are occasionally present. Small amounts of Ca, Mg, Fe^{+2} , Al, Zr, Mn, Be, Sn, Ti, Ta, yttrium earths and several percent silica may be present. Uranium is common, but rarely exceeds 0.5 weight percent (Overstreet, 1967). An elemental analysis for a nonmetamict monazite containing 15 percent UO_2 and 11 percent ThO_2 is presented in Table 23 (Gramaccioli and Segalstad, 1978). Thorium may be absent, as in the thorium free monazite from tin veins in Bolivia, or may reach 31.5 weight percent, as in a rare monazite from a pegmatite in India (Overstreet, 1967). Pavlenko, et al., (1965) report a silicomonazite containing approximately 40 weight percent Th. Traces of plutonium and neptunium have been reported in monazite and other uranium containing ores (Seaborg, 1958), Table 24.

Huttonite containing more than a trace of uranium is unknown. Attempts to synthesize uranium containing huttonite have produced thorite (Fron del and Collette, 1957; Mumpton and Roy, 1961).

OCCURRENCE

Monazite is widely distributed throughout the world as a detrital

Table 23: Chemical Composition (Rim) of uranium- and thorium-rich Monazite from Piona, Italy. Structural formula (right column) based on 16 oxygens (Gramaccioli and Segalstad, 1978).

	Weight Percent	Atomic Proportion	
FeO	trace		
CaO	4.45	0.742	
K ₂ O	0.71	0.140	
ThO ₂	11.34	0.401	
UO ₂	15.64	0.541	
Y ₂ O ₃	1.01	0.083	
La ₂ O ₃	13.89	0.796	3.856
Ce ₂ O ₃	16.31	0.928	
Pr ₂ O ₃	1.64	0.093	
Nd ₂ O ₃	2.34	0.130	
Dy ₂ O ₃	0.05	0.002	
P ₂ O ₅	31.02	4.082	
SiO ₂	0.16	0.025	4.107
Sum	98.56		

Not detected: Sc, Cr, Nb, Ta, Zr, Ga, Al, Ti, Mn, Na, Sm, Eu, Gd, Tb, Ho, Tm, Yb or Lu.			

Table 24: Concentration of Plutonium in Uranium Ores (Seaborg, 1958)

	U, wt.%	Pu/U ($\times 10^{12}$)
Canadian pitchblende	13.5	7.1
Belgian Congo pitchblende	38	12
Colorado pitchblende	50	7.7
Brazilian monazite	0.24	8.3
North Carolina monazite	1.64	3.6
Colorado fergusonite	0.25	4
Colorado carnotite	10	0.4

mineral in placer deposits and beach and river sands. It also occurs as a minor accessory mineral in metamorphic rocks, igneous rocks, pegmatites and vein deposits.

Monazite is found as a minor accessory mineral in metamorphosed argillaceous (clay containing) sediments and less commonly in metamorphosed arenaceous (sand containing) sedimentary rocks. It is common in pelitic schists, gneisses, and migmatites of medium to high grade metamorphism (amphibolite facies and granulite facies) (Overstreet, 1967). Thorium, rare earths and phosphorous dispersed primarily among the clays, mica, apatite and hydrolzates in the unmetamorphosed sediments are the source materials for the monazite in metamorphic rocks. As metamorphism progresses from low grade (greenschist facies) where monazite is rare to high grade (granulite facies), the thorium content of monazite increases, Table 25, (Overstreet, 1967).

The main monazite-bearing igneous rocks are granites which were emplaced during folding and high grade metamorphism of wall rocks (Overstreet, 1967). Monazite occurs in biotite-quartz-monzonite, two mica granite, biotite (a mica) granite, muscovite (a mica) granite, cassiterite (SnO_2) bearing granite, wolframite (monoclinic CaWO_4)-bearing granite and related pegmatite, greisen, and vein quartz. It commonly occurs in carbonatites and associated alkalic volcanic rocks and dikes. It is less common in diorite, granodiorite, quartz porphyry, aplite or felsite, and has been found in nepheline syenite and syenite pegmatite. It also occurs in veins and in cavities in rock which contained hydrothermal solutions. The thorium content of monazite in veins increases from epithermal (0.2 weight percent ThO_2) to mesothermal (1.4 weight percent ThO_2) to hypothermal veins, (3.4 weight percent ThO_2) (Overstreet, 1967).

Granitic batholiths contain monazite as an accessory mineral in small volumes. Carbonatites contain large concentrations of thorium-poor monazite while thorium-rich monazite is found in pegmatites. In plutons the concentration of thorium in monazite increases with increasing grade of metamorphism of the wall rocks,

Table 25: Thorium (ThO_2) Content of Monazite in Metamorphic Rocks
(Overstreet, 1967)

Metamorphic Grade of Host Rock	Metasedimentary Rocks (Weight Percent)	Metasedimentary Rocks & Migmatites (Weight Percent)
Greenschist	0.4	(')
Albite-epidote-amphibolite	3.0	(')
Amphibolite	4.9	6.1
Granulite	8.9	9.4

Not represented in analyses.

Table 26.

Concentration of monazite in sedimentary rocks is dominated by mechanical agents. Monazite and other heavy minerals are concentrated on beaches by the sorting action of waves and by shore currents (Borreswara, 1957). Extensive detrital deposits of monazite are found throughout the world.

Monazite, as pseudomorphs after apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F})$) have been reported in a deeply weathered pegmatite in Virginia. Rhabdophane (hexagonal CePO_4) occurs as an intimate mixture with the pseudomorphic monazite (Mitchell, Swanson and Crowley, 1976).

Cheralite ($((\text{Ce}, \text{La}, \text{Ca}, \text{Th})\text{PO}_4)$) occurs with black tourmaline (a borosilicate), chrysoberyl (BeAl_2O_4), dark zircon (ZrSiO_4), and smoky quartz in a kaolinized (altered to clay) pegmatite dike at Kuttakuzhi, Travancore, Southern India. Small amounts also occur in the adjacent wall rock (kaolinized granite-gneiss) and in surface wash.

Huttonite (monoclinic ThSiO_4) is quite rare in comparison with thorite (tetragonal ThSiO_4). It occurs as minute anhedral grains (0.2 mm) associated with scheelite (CaWO_4), cassiterite (SnO_2), uranothorite ($((\text{Th}, \text{U})\text{SiO}_4)$), zircon (ZrSiO_4), ilmenite (FeTiO_3), and gold in sands in Gillespie's Beach and at several other locations in Westland, New Zealand.

Silicomonazite ($((\text{Ce}, \text{La}, \text{Th}, \text{U})(\text{P}, \text{Si})\text{O}_4)$) occurs in placers, siltstone and sandstone. It forms intergrowths with quartz, orthoclase (KAlSi_3O_8), muscovite (a mica), hematite (Fe_2O_3) and occasionally with churchite (a hydrous RE-phosphate), rhabdophanite ($\text{CePO}_4 \cdot \text{H}_2\text{O}$), tapiolite (FeTa_2O_6) and xenotime.

Table 27 lists ages for some monazite occurrences. Reasonably concordant ages for samples over 2.0×10^9 years are known (Burger, et al., 1969) as are quite discordant ages for samples less than 3×10^8 years old (Stupnikova, et al., 1964). Postmineralization thermal events are frequently cited as causes for discordant ages.

Table 26: Thorium (ThO_2) Content in Monazite from Granite related to Probable Metamorphic Facies of Wallrock (Overstreet, 1967).

Metamorphic Facies of Predominantly Synorogenic Granite	Average Weight Percent Thorium (ThO_2)	Number of Analyses
Greenschist	0.47	1
Epidote-albite-amphibolite	6.8	1
Amphibolite		
Lower and middle subfacies	4.2	40
Middle and upper subfacies	6.0	43
Upper subfacies	6.0	92
Upper subfacies of Amphibolite facies and granulite facies	7.8	1

Metamorphic Facies of Cassiterite bearing Granite		
Greenschist	1.8	30
Albite-epidote-amphibolite	4.2	17
Amphibolite	6.9	15

Table 27: Radiometric Ages for Monazite Occurrences.

Occurrence	Age (m. y.)
1. Tara	1850
Posol-Angara	850
2. Manava	750
3. Azov	1997 $\pm$ 120
Ostropol (gray granite)	1800
(red pegmatite)	1500
Chernaya Salma	1700 $\pm$ 200
4. Naboomspruit	2050 $\pm$ 60
Brits	1950 $\pm$ 100
Kendal	1960 $\pm$ 90
Bandalierkop	2570 $\pm$ 90

1. Volobuev <u>et al.</u> (1963)	
2. Sastri and Sivaramakrishnan (1970)	
3. Kravchenko (1958)	
4. Burger <u>et al.</u> (1967)	

ALTERATION

Monazite persists in Precambrian sedimentary, igneous and metamorphic rocks. It is more resistant to intense chemical weathering than the minerals epidote ($\text{Ca}_2(\text{Al,Fe})_3\text{Si}_3\text{O}_{12}(\text{OH})$), garnet ($\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$), magnetite (Fe_3O_4) and apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH,F})$). Its abundance in placer deposits indicates monazite is a resistant mineral. Nonetheless, "monazite is often outwardly altered to or veined by fine-grained yellowish or reddish-brown products of unknown nature" (Fron del, 1958). Alteration to a dull earthy product through the removal of thorium and other components has been reported for a monazite from Brazil (Overstreet, 1967). Pavlenko *et al.* (1965) report a silicomonazite (approximate composition ThCePSiO_8) as unstable at low temperatures, nearly isotropic and intensively replaced by a fluorocarbonate even in "very fresh unaltered pegmatite". Cerianite (CeO_2) which is pseudomorphous after monazite has been reported by Neumann and Bergstol (1963). Burkser (1962) report monazite crystals with 0.5 mm crusts enriched in uranium (from the crystal) and in Pb^{204} (from the enclosing rock) by hypogene processes. Baranov (1961) reports that the uranium content of monazite increases with increasing degree of alteration.

RADIATION DAMAGE

Reports of radiation damaged monazite or huttonite are uncommon and in some cases suspect. Karkhanavala and Shankar (1954) report that annealing of 6 - 15 weight percent ThO_2 rich monazites at 1130°C sharpens the X-ray powder pattern, increases the density (5.33 to 5.62 g/cm^3 for 15 weight percent ThO_2), refractive indices (1.79 to 1.83) and birefringence. Ghouse (1968) observed that heat treatment at 1130°C of thorium-rich monazite causes powder lines to sharpen and increase in number and intensity. He also concludes that because of radiation damage considerable distortion remains in the monazite structure after annealing; a conclusion based on an incorrect structure refinement. A "silicomonazite" was described by Nekrasov,

(1971) as 20 - 30 percent metamict. The structure was restored by heating at 850°C for 4 hours. Zimmerle (1971) reports two generations of monazite from quartz-chlorite veinlets of hydrothermal origin in Belgium. The older monazite is metamict; the younger monazite is unaltered.

A hydrothermal huttonite has been reported as metamict by Kosterin and Zuev (1962), but otherwise huttonite has not been found in the metamict state. Thorite (ThSiO_4) (and zircon, ZrSiO_4) are frequently metamict. Thorite and zircon become about 15 percent less dense during their transition from crystalline to metamict state (Holland and Gottfreid, 1955).

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URANINITE GROUP: UO_2 , ThO_2 , CeO_2

Uraninite group minerals are analogues for the supercalcine fluorite phase, $(\text{U,Ce,Zr,RE})\text{O}_{2+x}$. Fluorite-type phases are highly resistant to radiation damage. ThO_2 is durable and UO_2 is durable under reducing conditions. The geochemical behavior of UO_2 is complex.

MINERAL DATA

Mineral data for uraninite group minerals are as follows:

Formula:	Uraninite (UO_{2+x})	Cerianite (CeO_2)
Crystal System:	Cubic	Cubic
Space Group:	Fm3m	Fm3m
Z:	4	4
Lattice Constant:	$a = 5.40 - 5.55 \text{ \AA}$	$a = 5.42 - 5.50 \text{ \AA}$
Mohs Hardness:	5 - 6	(?)
Density (gm/cm^3):	6.5 - 11.0	5.89 - 6.03

Formula:	Thorianite (ThO_2)
Crystal System:	Cubic
Space Group:	Fm3m
Z:	4
Lattice Constant:	$a = 5.57 - 5.59 \text{ \AA}$
Mohs Hardness:	6 1/2 - 7
Density (gm/cm^3):	9.7 - 10.0

STRUCTURE

The dioxides of uranium, thorium and cerium have the fluorite structure. Oxygen ions form a simple cubic packed lattice and cations occupy one half of the interstitial voids. Each cation coordinates with a cubic arrangement of eight oxygen ions. The resulting MO_8 cubes form an edge sharing network.

The most striking property of the fluorite type structure is the extent to which it can incorporate cations of different charges. The resulting mixed valence crystals have a defect fluorite structure. Charge balance is thought to be retained by anion vacancies or by the presence of interstitial anions (Bevan and Kordis, 1964).

Makarov et al. (1960) have, on the basis of neutron powder diffraction data, proposed that oxygen rich pitchblendes (UO_{2+x}) of composition $\text{UO}_{2.33}$ have $\text{Pa}3$ space group symmetry instead of the fluorite structure. The deviation would be a result of the presence of UO_2^{+2} ions, which are covalent units. The resulting short U-O bonds cause some oxygen atoms to deviate from their special positions occupied in the fluorite structure.

CHEMISTRY

The stoichiometric dioxide systems $\text{UO}_2\text{-ThO}_2$, $\text{CeO}_2\text{-ThO}_2$ and $\text{UO}_2\text{-CeO}_2$ show complete miscibility at room temperature (Slowinski and Elliott, 1952; Hoch and Yoon, 1964; Markin, Street and Crouch, 1970). The corresponding nonstoichiometric oxide systems are more complicated, having extensive two phase regions when oxygen rich or deficient.

Phase equilibria in the Ce-O system have been studied by Bevan and Kordis (1964), and Brauer et al. (1960). The CeO_{2-x} fluorite phase has a defect structure (anion vacancies) when oxygen deficient. At temperatures below 636°C the fluorite phase may have a composition ranging from CeO_2 to $\text{CeO}_{1.82}$. At increased temperatures

(685–1023°C) the fluorite phase extends the composition range from CeO_2 to $\text{CeO}_{1.72}$.

CeO_2 may also incorporate significant amounts of other rare earth oxides into its structure. Neumann and Bergstol (1963) reported a natural cerianite (CeO_2) which contained 30 – 35 weight percent RE_2O_3 . Zintl and Crotto (1939) indicates that CeO_2 - La_2O_3 solid solutions containing up to 44 percent La_2O_3 have the fluorite structure.

Hoekstra et al. (1970) studied the U-O system in the composition range UO_2 – UO_3 , Figure 26. At elevated temperatures one fluorite type phase is observed in the composition range UO_2 - $\text{UO}_{2.25}$. At lower temperatures one fluorite phase and a fcc phase (U_4O_9) are observed. Others (Schaner, 1960; Young et al., 1962) report that the UO_{2+x} fluorite phase may be quenched without phase separation. Naturally occurring uraninites have a much broader variation in oxygen content than synthetic UO_{2+x} . Naturally occurring uraninites may have a composition near $\text{UO}_{2.6}$ and still retain the fluorite structure. If these oxygen rich uraninites are annealed in a vacuum, the x-ray powder diffraction lines due to UO_2 sharpen and increase in intensity. Diffraction lines due to U_3O_8 sometimes appear after annealing (Brooker and Nuffield, 1952). As the UO_3 content of uraninite increases, the unit cell edge decreases (Harshman, 1970).

Unlike CeO_{2-x} and UO_{2+x} , cation pure ThO_2 does not form nonstoichiometric oxides although it can incorporate ions with a charge other than +4 in its structure. The ThO_2 - UO_2 -O system has been studied by Sata (1965) and Cohen and Berman (1966). The system is found to have a fluorite phase, $\text{U}_{1-z}\text{Th}_z\text{O}_{2+x}$ with a range of values of z and x . Only minor amounts of ZrO_2 are soluble in the ThO_2 fluorite structure (Mumpton and Roy, 1959; Evans, 1960; Romberguer et al., 1967). Major amounts of CaO can be incorporated into the thorianite crystal structure. Andreev and Maslov (1966) report a natural thorianite (ThO_2) which contained 20 mole percent CaO.

The Th-Ce-O system has been investigated by Hoch and Yoon (1964). Up to 45 mole percent $\text{CeO}_{1.5}$ is soluble in the thorianite

Figure 26: A phase diagram for the UO_2 - UO_3 system (Hoekstra et al., 1970).

structure. The system $\text{CeO}_2\text{-Ce}_2\text{O}_3\text{-ThO}_2$ has a large two phase region where two defect fluorite structures coexist. The defect phases become miscible near the $\text{CeO}_2\text{-ThO}_2$ line.

The U-Ce-O system has been studied over the range $\text{UO}_2\text{-U}_3\text{O}_8$ and $\text{CeO}_2\text{-CeO}_{1.818}$ by Markin et al. (1970). Two fluorite phases are observed when oxides of composition $\text{U}_{1-z}\text{Ce}_z\text{O}_{2+x}$, $z > .35$, are partially reduced. If $z < .35$, then partial reduction of the oxide results in a single oxygen deficient fluorite MO_{2-x} phase. For oxides with $z < .5$, partial oxidation results in either a single MO_{2+x} phase or MO_{2+x} and M_4O_9 phases. Further oxidation causes the MO_{2+x} phase to disappear and an equilibrium to be established between M_4O_9 and M_3O_8 phases.

OCCURRENCE

Thorianite (ThO_2) and other thorium minerals occur originally as accessory minerals in igneous rocks and in hydrothermal veins. The major types of deposits of thorium minerals are listed in Table 28. Thorium minerals are normally resistant to weathering, abrasion and alteration; therefore they tend to outlast surrounding rocks and become concentrated in detrital deposits. Monazite (CePO_4), not thorianite or thorite (ThSiO_4) is the major thorium mineral. By comparison with uraninite, thorianite is an uncommon mineral.

Thorianite tends to crystallize from magmatic fluids at higher temperatures, pressures and at greater depths than uraninite (UO_2). Nonetheless thorianite-uraninite solid solutions span the entire range of possible compositions in $(\text{Th,U})\text{O}_2$ of magmatic or pegmatitic origin.

Different weathering characteristics of uranium and thorium minerals cause U and Th to become segregated. Thus when uranium is leached and redeposited as pitchblende at low temperatures it usually has less than 1 weight percent ThO_2 or RE_2O_3 . Uraninite quickly oxidizes under present surface conditions although in the reducing atmosphere of Precambrian times it was sufficiently durable to form placer deposits (Brobst and Pratt, 1973). Vein deposits and igneous

Table 28: The Principal Types of Thorium Deposits (Brobst and Pratt, 1973).

Type of deposit	Host rock	Thorium minerals--minerals	Origin
Veins	Frequently associated with alkalic complexes and carbonatites.	Monazite, thorianite, thorite, allanite, brockite, (U,Th)-minerals.	Deposited from mobile fluids at low temperatures.
Placers	Beach and stream deposits of detrital minerals.	Monazite, thorianite, thorite, and uranothorite, other detrital minerals.	Durable thorium minerals which outlast surrounding igneous rocks.
Sedimentary rock	Fossil placer deposits frequently as sandstones or conglomerates.	Monazite, thorium and uranium minerals and other detrital minerals.	As above.
Metamorphic and igneous rocks	In granitic complexes, alkalic complexes, carbonatites and metamorphic rocks from garnet to sillimanite grade.	Principally monazite.	

rocks are the original sources of uranium minerals, but hydrothermal deposits are the most important. Table 29 lists the important types of uranium deposits.

Granitic rocks appear to be important sources of uranium for hydrothermal deposits because: 1) they are enriched in uranium, over 5 ppm, 2) they contain only minor amounts of reducing agents to retard the oxidation of relatively insoluble U^{+4} to the soluble U^{+6} species, and 3) much of the uranium content of granitic rocks occurs as easily removed stains and thin films on rock grains (Rich, Holland and Petersen, 1977; Brobst and Pratt, 1973). Experimental work by Szalazy and Samsoni (1969) and Larsen et al. (1956) indicate that uranium is easily leached from granitic rocks by dilute acid. It has been reported that under surface weathering conditions at least 50 weight percent of the uranium content of granitic rocks is leachable (Barbier, 1974; Barbier and Ranchin, 1969). Uraninite, biotite and hornblende are considered to be sources of easily leached uranium in granitic rocks (Rich, Holland and Petersen, 1977). Gabelman (1977) agrees that leaching of uranium from igneous rocks occurs but presents evidence indicating that the greatest quantities of uranium are mobilized after rock destruction.

Once leached, uranium is carried in the water soluble +6 oxidation state, possibly as $UO_2(CO_3)_2^{-2}$ in neutral solutions or as $UO_2(CO_3)_3^{-4}$ in alkaline solutions (Hostetler and Garrels, 1962). Uranium is transported in this manner until a reducing environment is encountered, causing precipitation as pitchblende, UO_{2+x} , (Harshman, 1970), or coffinite ($USiO_4$) (Brookins, 1976). H_2S , ferrous iron (Fe^{+2}), and organic carbon are frequently mentioned reducing agents (Rich, Holland and Petersen, 1977; Harshman, 1970). Clays and organic material adsorb significant amounts of uranium from solution. The geology and chemistry of uranium dissolution, transport and precipitation by and from aqueous solution are subjects of intense study. References intended to introduce the reader to this literature are included in the bibliography.

Table 29: The Principal Types of Uranium Deposits (Brobst and Pratt, 1973).

Type of deposit	Host rock	Uranium minerals--minerals	Origin
Peneconcordant	Typically quartz rich sandstone interbedded with mudstone containing organic material.	Uraninite, coffinite or secondary uranium minerals.	Precipitation of uranium from ground water at low temperatures and pressures.
Quartz-pebble conglomerates	Fossil deposits of detrital minerals.	Uraninite, brannerite, pyrite, thorium minerals and other detrital minerals.	Durable uranium minerals from igneous rock which was eroded in Precambrian times (low P ₀₂ atmosphere).
Vein deposits	Fissure fillings in faults and fracture zones in a variety of host rocks, sometimes host rock is partially replaced as well.	Uraninite, thorium minerals, fluorite and base-metal sulfides.	Hydrothermal solutions derived from magmas.
Uraniferous igneous rocks	Pegmatites (usually zoned) and granites, pyrochlore bearing alkalic rocks, nepheline syenites, sodalite foyaites.	Primary uranium ore minerals, thorium minerals.	Magmas.
Phosphatic rocks	Marine phosphorite,	Apatite.	U deposited from sea water during sedimentation.
Marine black shales	Shale containing organic matter.		Uranium deposited along with organic matter in shale.

Table 30 lists the more significant minerals of uranium and thorium. Thorium minerals are generally phosphates, silicates or oxides while uranium occurs as a wide variety of minerals.

Cerianite, CeO_2 , is unique among rare earth containing minerals in that Ce is present in the +4 oxidation state. It is thought to be a weathering or alteration product of Ce^{+3} minerals.

Cerianite from a granite pegmatite in Norway is pseudomorphic after monazite (Neumann and Bergstol, 1963). This occurrence is associated with fluorocerite $((\text{Ce}, \text{La})\text{F}_3)$, bastnaesite $((\text{Ce}, \text{La})\text{CO}_3\text{F})$, tornebohmitite $(\text{RE}_3(\text{SiO}_4)_2(\text{F}, \text{OH}))$ and monazite, CePO_4 . In this case the monazite was oxidized to cerianite and then partially reduced to fluorocerite. Cerianite as minute octahedral crystals were found at the interfaces of silicate rich inclusions and impure sugary carbonate rock in a nephelinized hybrid gneiss in Ontario (Graham, 1955). Apatite $(\text{Ca}_5(\text{PO}_4)_3\text{F})$, magnetite (Fe_3O_4) , ilmenite (FeTiO_3) , nepheline $(\text{NaAlSi}_3\text{O}_8)$, feldspar $((\text{Na}, \text{K}, \text{Ca})\text{AlSi}_3\text{O}_8)$, brown tremolitic amphibole and accessory fluorite (CaF_2) are associated with this cerianite occurrence. In a perrierite bearing pegmatite in Virginia, cerianite occurs as an intimate mixture with monazite, rhabdophane (hexagonal CePO_4) and halloysite (Mitchell et al., 1976). Table 31 gives the chemical compositions of two cerianites. Table 32 lists representative radiometric ages for uraninite occurrences.

ALTERATION

Uraninite is unstable at surface conditions. When exposed to weathering, brightly colored secondary minerals are formed. All of the uranium minerals listed in Table 31 with the exceptions of the oxides, multiple oxides, and silicates are alteration products of uraninite. Most of the secondary minerals are soluble and none are sufficiently durable to form significant detrital deposits (Nininger, 1954).

Thorianite ThO_2 is normally very resistant to weathering, but its resistance is lowered if it contains significant amounts of uranium

Table 30: A List of the More Important Uranium and Thorium Bearing Minerals (Beckerley, 1956).

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Oxides	Uraninite (pitchblende), UO_2 .	Thorianite, ThO_2 .
Hydrous oxides	Gummite, $\text{UO}_3 \cdot n\text{H}_2\text{O}$;	
Multiple oxides	Brannerite, $(\text{U}, \text{Ca}, \text{Fe}, \text{Th}, \text{Y})_3 \text{Ti}_5 \text{O}_{16}$; Davidite, $(\text{Fe}, \text{Ce}, \text{U})(\text{Ti}, \text{Fe}, \text{V}, \text{Cr})_3 (\text{O}, \text{OH})_7$.	Yttrocrasite, $(\text{Y}, \text{Th}, \text{U}, \text{Ca})_2 (\text{Ti}, \text{Fe}, \text{W})_4 \text{O}_{11}$; Zirkelite, $(\text{Fe}, \text{Th}, \text{U}, \text{Ca})_2 (\text{Ti}, \text{Zr}) \text{O}_5$.
Silicates	Coffinite, $\text{U}(\text{SiO}_4)_{1-x} (\text{OH})_{4x}$.	Thorite, ThSiO_4 .
Hydrous silicates	Uranophane, $\text{CaO} \cdot 2\text{UO}_3 \cdot 2\text{SiO}_2 \cdot 6\text{H}_2\text{O}$; Beta-uranotile, $\text{CaO} \cdot 2\text{UO}_3 \cdot 2\text{SiO}_2 \cdot 6\text{H}_2\text{O}$ Sklodowskite, $\text{MgO} \cdot 2\text{UO}_3 \cdot 2\text{SiO}_2 \cdot 6\text{H}_2\text{O}$.	Thorogummite, $\text{Th}(\text{SiO}_4)_{1-x} (\text{OH})_{4x} (?)$
Hydrous phosphates	Autunite, $\text{CaO} \cdot 2\text{UO}_3 \cdot \text{P}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$; Torbernite, $\text{CuO} \cdot 2\text{UO}_3 \cdot \text{P}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$.	
Anhydrous phosphates		Monazite, $(\text{Ce}, \text{Y}, \text{La}, \text{Th})\text{PO}_4$; Xenotime, $(\text{Y}, \text{Th})\text{PO}_4$.
Hydrous arsenates and vanadates	Zeunerite, $\text{CuO} \cdot 2\text{UO}_3 \cdot \text{As}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$; Carnotite, $\text{K}_2\text{O} \cdot 2\text{UO}_3 \cdot \text{V}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$; Tyuyamunite, $\text{CaO} \cdot 2\text{UO}_3 \cdot \text{V}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$.	
Hydrous sulfates	Zippeite, $2\text{UO}_3 \cdot \text{SO}_3 \cdot n\text{H}_2\text{O}$; Uranopilite, $6\text{UO}_3 \cdot \text{SO}_3 \cdot n\text{H}_2\text{O}$; Johannite, $\text{CuO} \cdot 2\text{UO}_3 \cdot 2\text{SO}_3 \cdot 7\text{H}_2\text{O}$.	
Carbonates	Schroëckerite, $3\text{CaO} \cdot \text{Na}_2\text{O} \cdot \text{UO}_3 \cdot \text{CO}_2 \cdot \text{SO}_3 \cdot 10\text{H}_2\text{O}$	

Table 31: Chemical Compositions for Cerianite from Three Occurrences.

Oxide	Weight Percent		
	1.	2a.	2b.
SiO ₂	n.d.	1.89	1.56
Al ₂ O ₃	n.d.	2.20	0.22
Y ₂ O ₃	1.2	0.10	0.10
La ₂ O ₃	1.5	15.10	20.80
CeO ₂	80	55.80	51.90
Pr ₂ O ₃	n.d.	4.60	4.30
Nd ₂ O ₃	n.d.	9.80	10.50
Sm ₂ O ₃	n.d.	1.10	1.50
Gd ₂ O ₃	n.d.	0.15	0.30
ThO ₂	5.1	1.80	1.60
CaO	n.d.	1.67	1.05
MgO	n.d.	0.05	0.23
F	n.d.	2.51	2.55
Nb ₂ O ₅	1.8	n.d.	n.d.
Yb ₂ O ₃	1.1	n.d.	n.d.
Ta ₂ O ₅	0.6	n.d.	n.d.
ZrO ₂	0.6	n.d.	n.d.

1. Graham (1955)

2. Neumann and Bergstol (1963)

Table 32. Radiometric Ages for some Uraninite Occurrences.

Location	Age (m. y.)
1. South Crofty, Cornwall	277 $\pm$ 10
Geevor, Cornwall	223 $\pm$ 5
King's Wood, Devon	206 $\pm$ 5
Wheal Bray, Cornwall	165 $\pm$ 4
South Terras, Cornwall	47 $\pm$ 2
Geevor, Cornwall	45
2. Outokumpo, Finland	1850
3. Southwest Sweden	930
Northern Sweden	1810
4. Yamaguchi Mine, Japan	94
Iisaka, Japan	98
Masaki, Japan	111
5. Bhunas Mine, Rajasthan (India)	906 $\pm$ 20
1. Darnley <u>et al.</u> (1965)	
2. Wetherill <u>et al.</u> (1962)	
3. Welin and Blomquist (1964)	
4. Sato and Saito (1964)	
5. Choudari <u>et al.</u> (1967)	

(Nininger, 1954). Studies on the weathering of bedrock containing both uranium and thorium indicate that uranium leaches more quickly than thorium (Titaeva and Veksler, 1969). Under hydrothermal conditions ThO_2 will react with quartz to give ThSiO_4 .

In contrast to uranium, thorium has only one oxidation state which occurs under geologic conditions. Therefore, dissolution of thorium minerals as a result of redox reactions is not observed in nature. Nevertheless, thorium is soluble under magmatic-hydrothermal conditions at moderate to high temperatures (above 600–750°C). Under these conditions thorium may be mobile as an ion, ThF_6^{-2} , or molecule, ThF_4 (Scherbina and Abakirov, 1967; Gabelman, 1977).

Both the +4 and +6 oxidation states of uranium are observed in nature. The +4 oxidation state is stable under reducing conditions. Uranium is soluble as U^{+4} in solutions having a pH of 3 or less, in the presence of CO_2 and mild oxidizing conditions (Hostetler and Garrels, 1962). Under the proper Eh and pH conditions, uraninite is quite insoluble (Langmuir, 1978), Figures 27a and 27b. According to Langmuir (1978), uraninite is somewhat soluble in the presence of carbonate in solutions with Eh – pH ranges of 0.2 volts and pH 5 to 0.0 volts and pH 8. Hostetler and Garrels (1962) indicate that the stability field of uraninite in the $\text{U-O}_2\text{-CO}_2\text{-H}_2\text{O}$ system is considerably more restricted than Langmuir proposes, Figure 27a. Figure 27b is a plot of uraninite solubility vs. Eh at pH 8 (Langmuir, 1978).

The kinetics of uraninite dissolution have been studied by Grandstaff (1976). Although further kinetic studies are needed, the following results were indicated:

- 1) The dissolution rate is proportional to the surface area.
- 2) There is no significant correlation between the rate of dissolution and the ratio $\text{U(IV)}:\text{U(VI)}$.
- 3) The presence of thorium in uraninite decreases the rate of dissolution.
- 4) The dissolution rate is first order with respect to $\text{P(O}_2\text{)}$, for $T = 23^\circ\text{C}$ and $\text{P(O}_2\text{)}$ less than 0.2 atm.

(a)

(b)

Figure 27: a) An Eh - pH diagram of the system U-O-CO₂-H₂O at 25°C and $P(\text{CO}_2) = 10^{-2}$ atm. H & G denotes the uraninite stability field according to Hostetler and Garrels (1962) (Langmuir, 1978).

b) The solubility of uraninite at pH 8 and $T = 25^\circ\text{C}$ as a function of Eh and $P(\text{CO}_2)$ (after Langmuir, 1978).

- 5) The rate of dissolution is first order with respect to hydrogen ion concentration, at least in the pH range 4 to 6.
- 6) At low carbonate concentrations there is a first order dependence on total carbonate concentration.
- 7) Organic material retards the rate of dissolution of uraninite.

RADIATION DAMAGE

Uraninite, thorianite and cerianite have been called metamict (Hurley and Fairbain, 1953; Neumann and Bergstol, 1963); a term probably not deserved by these minerals (Brooker and Nuffield, 1952). Note that the $^{238}\text{PuO}_2$ analogue to uraninite does not appear to suffer a fundamental loss of crystallinity (i.e. does not become metamict) although it is affected by radiation damage (Turcotte, 1976). So called metamict pitchblende or cerianite is probably ordinary pitchblende or cerianite. Commonly pitchblende is fine grained and poorly crystalline. Its x-ray amorphous character probably is a result of ultra-small crystallite sizes and not a result of radiation damage. Although these minerals may occur in the metamict state, this conclusion requires more evidence than simple x-ray diffraction studies.

URANINITE

Structure

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"HOLLANDITE"-PRIDERITE: $(K,Ba)_{2-x}(Fe,Ti)_8O_{16}$

Priderite is an analogue for the SYNROC "hollandite" phase $(Ba,Cs)_{2-x}(Al,Ti)_8O_{16}$. Priderite is isostructural with the manganese oxide mineral hollandite. Priderite is an extremely rare mineral which occurs in leucite bearing rocks in one region of Australia. Priderite may be durable, but it is not a good compositional analogue for "hollandite".

MINERAL DATA

Mineral Data for priderite are as follows:

Formula: $(\text{K}, \text{Ba})_{2-x}(\text{Fe}, \text{Ti})_8\text{O}_{16}$

Crystal System: Tetragonal

Space Group: $I4/m$

Z: 1

Lattice Constants: $a = 10.11$

Density (gm/cm^3): 3.86

STRUCTURE

The crystal chemistry of hollandite type phases is complex. The idealized hollandite, $A_x M_8(O,OH)_{16}$ ($x \leq 2$), structure is tetragonal with $Z = 1$ and $I4/m$ space group symmetry. The A site ions can be alkali, alkali earth, Ag, Tl and Pb while M site ions are Mg, Zn, Ga, In, Si, Ge, Sn, Sb and many of the first row transition elements (Pentlinghaus, 1978). The SYNROC "hollandite" is a phase with approximate composition: $(Ba,K)_{2-x}(Ti,Al)_8O_{16}$. M site ions are in octahedral coordination by O. MO_6 octahedra share three edges to form double chains along the c-axis. Each double chain links with four other double chains by sharing corners to form two large tunnels per unit cell. The large tunnels are coincident with four fold rotation axes. Potassium and barium occupy the tunnels, and have $4/m$ site symmetry. A-site ions are surrounded by an approximate cube of oxygens with a O distance of 2.74 Å. Four other oxygens bisect the sides of the cube and have a M-O distance of 3.31 Å. Some hollandites are slightly distorted from the idealized tetragonal structure (Bystrom and Bystrom, 1950). A diagram of the hollandite structure is given in Figure 28. The rutile structure is similar in that it is composed of edge sharing chains that parallel the C axis. In rutile each TiO_6 octahedron shares only two edges, hence rutile structure is composed of single and not double chains. The tunnels in the rutile structure are about one-fourth the cross-sectional area of the large tunnels in the hollandite structure. Crystallographic data are given for some hollandite structure phases in Table 33. Ringwood and co-workers have recently refined the crystal structure of Ba-titanate hollandite.

CHEMISTRY

According to Ringwood et al. (1979) there is "extensive" solid solution among $K_2Al_2Ti_6O_{16}$, $Na_2Al_2Ti_6O_{16}$, $SrAl_2Ti_6O_{16}$, $BaAl_2Ti_6O_{16}$ and $(CsAl)_{2-x}Ti_{6+x}O_{16}$. The stoichiometric compound $Cs_2Al_2Ti_6O_{16}$ does not exist, presumably because the ion diameter of Cs^+ exceeds the c axis repeat distance (Bayer and Hoffman, 1966). Hollandite phases

Figure 28. A representation of the hollandite or priderite structure. Open circles denote ions at the level $z = 0$ and filled circles ions at $z = \frac{1}{2}$ (Bystrom and Bystrom, 1950).

Table 33: Crystallographic data for hollandites. All are tetragonal (I4/m) with Z = 1.

	a(A)	c(A)	density (gm/cm ³)
1. Na ₂ (Al ₂ Ge ₆)O ₁₆	9.6515	2.8551	4.94
2. K ₂ (Al ₂ Ge ₆)O ₁₆	9.7058	2.8611	5.07
3. K ₂ (Ga ₂ Ge ₆)O ₁₆	9.7810	2.8879	5.46
4. K ₂ (Al ₂ Ti ₆)O ₁₆	10.040	2.940	
5. K _{1.6} (Al _{1.6} Ti _{6.4})O ₁₆	10.067	2.939	
6. K ₂ (Cr ₂ Ti ₆)O ₁₆	10.125	2.955	
7. K ₂ (Fe ₂ Ti ₆)O ₁₆	10.148	2.969	
8. K ₂ (MgTi ₇)O ₁₆	10.157	2.974	
9. K ₂ (CoTi ₇)O ₁₆	10.139	2.975	
10. K ₂ (NiTi ₇)O ₁₆	10.140	2.965	
11. K ₂ (CuTi ₇)O ₁₆	10.135	2.977	
12. K ₂ (ZnTi ₇)O ₁₆	10.161	2.973	
13. Rb ₂ (Al ₂ Ti ₆)O ₁₆	10.102	2.941	
14. Rb ₂ (Cr ₂ Ti ₆)O ₁₆	10.168	2.957	
15. Rb ₂ (Fe ₂ Ti ₆)O ₁₆	10.189	2.976	
16. Rb ₂ (MTi ₇)O ₁₆	10.191-10.203	2.967-2.980	

M = Mg,Co,Ni,Cu, or Zn

1 - 3 Pentinghaus, 1978

4 - 16 Bayer and Hoffman, 1966

including priderite $(\text{K,Ba})_x(\text{Ti,Fe})_8\text{O}_{16}$ are frequently nonstoichiometric.

It is notable that SYNROC-"Ba-Hollandite", $\text{BaAl}_2\text{Ti}_6\text{O}_{16}$ does not occur as a mineral. The mineral priderite is essentially a K-Fe-titanate with significant amounts of Ba and Al. The chemical composition of priderite from the Kimberly area of Australia is given in Table 34.

OCCURRENCE AND ALTERATION

Priderite is a mineralogic oddity. It occurs in leucite (KAlSi_2O_6) bearing volcanic rocks in the Kimberly region of Western Australia. Minerals associated with priderite include: leucite, phlogopite (a mica), diopside ($\text{CaMg}(\text{SiO}_3)_2$), rutile, amphibole, serpentine, calcite, barite (BaSO_4), zeolites, accessory wadeite, perovskite and apatite. Optical properties of priderite closely resemble those of rutile and on the basis of microscopy, priderite can be mistaken for rutile.

It is highly probable that priderite and $\text{BaAl}_2\text{Ti}_6\text{O}_{16}$ are unstable with silicate rocks such as quartz and alkali feldspars. The mineral is too rare to infer from the geologic literature anything about its weathering and alteration characteristics. Structural and compositional differences make rutile a poor analogue for "hollandite".

Table 34: Chemical composition of priderite.

	1.	2.	3.
TiO ₂	65.3	65.4	70.6
Fe ₂ O ₃	-	21.8	12.4
Al ₂ O ₃	13.8	-	2.3
BaO	20.9	-	6.7
K ₂ O	-	12.8	5.6
Na ₂ O	-	-	0.6
CaO	-	-	trace
Total	100.0	100.0	98.2

1. Ideal composition of BaAl₂Ti₆O₁₆

2. Ideal composition of K₂Fe₂Ti₆O₁₆

3. Priderite of Kimberly area (K_{.87}Ba_{.32}Na_{.14})(Fe³⁺_{1.14}Al_{.33})Ti_{6.48}O₁₆
(Norrish, 1951).

HOLLANDITE (PRIDERITE)

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PEROVSKITE: CaTiO_3 , $(\text{Ca,RE,Th})_{1-x}\text{TiO}_3$.

Varieties of perovskite are close natural analogues to the SYNROC perovskite phase, $(\text{Ca,RE})_{1-x}\text{TiO}_3$. Perovskite is subject to radiation damage. It is durable in silica undersaturated rocks.

MINERAL DATA

Mineral data for perovskite are as follows:

Formula: CaTiO_3 (ideal) or $(\text{Ca,Na,RE,Th})(\text{Ti,Nb})\text{O}_3$

Crystal System: Pseudocubic

Space Group: $\text{Pm}\bar{3}\text{m}$ (idealized)

Z: 1 (idealized cubic cell)

Lattice Constants: Pseudocubic cell $a \sim 3.8 \text{ \AA}$

Mohs Hardness: 5 1/2

Density (gm/cm^3): 3.98 - 4.26

STRUCTURE

A large number of ABO_3 compounds have the same structure as perovskite, $CaTiO_3$. Crystallographic data for some titanates, zirconates, niobates, aluminates and other compounds with the perovskite structure are given in Table 35.

In the perovskite structure, Figure 29, TiO_6 octahedrons are linked to form a three dimensional network in which all octahedron corners are shared. There is one large cubo-octahedral void per TiO_6 octahedron. This void, which is bounded by twelve oxygen atoms, is occupied by calcium. The idealized perovskite structure is cubic with $Pm3m$ space group symmetry. Most perovskite type compounds are slightly distorted and are pseudo-cubic, belonging to monoclinic, orthorhombic, tetragonal or rhombohedral crystal classes.

CHEMISTRY

In the perovskite structure, atoms such as Na, K, Ca, Sr, Ba, Cd, REE and Th can substitute for Ca. Smaller atoms such as Al, Fe^{+3} , and Nb may substitute for Ti. In natural perovskite, Nb is the only element which will substitute for Ti to any significant extent. Lueshite, $NaNbO_3$, is an end-member variety of perovskite in which substitution of Na^+ for Ca^{++} is compensated for replacement of Ti^{+4} by Nb^{+5} . Perovskite commonly contains up to a few wt% Na, REE and Sr but usually less than 1 wt% ThO_2 . Perovskite usually contains less than 3 wt% Fe^{+2} , Al and Si. Frank-Kamenetskii and Vesel'skii (1961) suggest that Si, Al and in part Fe are not structural and point out that their exclusion often improves stoichiometric relations. Irinite and loparite are nearly Ca free varieties of perovskite which can contain 27 wt% REE and 13 wt% ThO_2 . The major means of accommodating substitution of rare earth elements are: 1) deviation from ideal ABO_3 stoichiometry and 2) coupled replacements such as $REE^{+3} + Na^+ \rightleftharpoons Ca^{+2} + Ca^{+2}$. Compositions for a number of perovskites are given in Table 36. There is complete solid solution in

Table 35: Crystallographic data for a few compounds with the perovskite structure.

	Space Group or Bravais Lattice	a.	b.	c.	β	Z	
1. NaNbO_3 (Cubic above 640°C)	monoclinic-P	3.91	3.91	3.91	90	1	4.55
2. KNbO_3	cubic-P	4.015	-	-	-	1	-
3. CaTiO_3	Pnma	5.4405	7.6436	5.3812	-	4	4.036
4. CdTiO_3	orthorhombic	10.615	7.615	10.834	-	16	-
5. SrTiO_3	Pm3m	3.9051	-	-	-	1	5.116
6. BaTiO_3 (Cubic above 120°C)	P4mm	3.994	-	4.038	-	1	-
7. CaZrO_3	cubic-P	4.10	-	-	-	1	-
8. SrZrO_3	Pnma	5.814	8.196	5.792	-	4	5.458
9. BaZrO_3	Pm3m	4.193	-	-	-	1	-
10. CeAlO_3	cubic-P	3.767	-	-	-	1	-
11. CeAlO_3 (Cubic above 500°C)	rhombohedral	3.779	-	-	≈ 90.13	1	-
12. TbAlO_3	Pnma	5.3097	7.4196	5.2317	-	4	-
13. BaCeO_3	orthorhombic	8.779	6.214	6.236	-		
14. BaThO_3	Pm3m	4.495	-	-	-	1	
15. CeFeO_3	orthorhombic	5.577	7.809	5.541	-	4	6.714
16. LaCrO_3	Pnma	5.513	7.756	5.479	-	-	-

JCPDS, Powder Diffraction File Number or Reference

1. 19 - 1221	6. 5 - 626	11. Mosley, 1971	16. 24 - 1016
2. 8 - 212	7. 20 - 254	12. 24 - 1270	
3. 22 - 153	8. 10 - 268	13. 22 - 74	
4. 3 - 818	9. 6 - 399	14. 3 - 1102	
5. 5 - 634	10. 28 - 260	15. 22 - 166

Figure 29. Polyhedral representation of the perovskite structure (Bloss, 1971).

Table 36. Chemical Compositions of Varieties of Perovskite

	1.	2.	3.	4.	5.	6.
CaO	41.8	25.95	36.31	26.55	1.47	1.83
TiO ₂	58.2	10.05	53.87	51.47	39.28	46.45
Nb ₂ O ₅	-	43.90	0.36	2.50	3.95	6.31
Fe ₂ O ₃	-	* 8.74	1.77	1.87		0.88
Na ₂ O	-	4.03	1.29	1.74	6.36	6.41
K ₂ O	-	0.03	0.51	0.45	0.54	-
REE	-	2.03	2.58	10.70	31.28	24.00
MgO	-	2.20	Tr	Tr	-	-
MnO	-	0.77	-	-	0.02	-
SiO ₂	-	0.45	1.70	1.15	8.18	-
S	-	0.90				-
Te ₂ O ₃	-	-			2.46	
ThO ₂	-	-	0.08	0.08	3.00	13.00
U ₃ O ₈	-	-	-	-	0.17	-
SrO	-	-	1.18	1.63	1.21	-
ZrO ₂	-	-	Tr	-	0.10	-
Al ₂ O ₃	-	-	-	1.30	0.60	-
Water of hydr.	-	-	-	0.17	0.54	-
L.O.I.	-	0.65	0.56	0.45	-	1.25
Total	100.0	99.70	100.22	99.73	-	-

-
1. Ideal composition of CaTiO₃
 2. Niobian perovskite (Nickel and McAdam, 1963)
 3. Perovskite (Frank-Kamenetskii and Vesel'skii, 1961)
 4. Rare earth bearing perovskite (Frank-Kamenetskii and Vesel'skii, 1961)
 5. Loparite (Gorzhevskaya and Sidorenko, 1969)
 6. Irinite (Borodin and Kazakova, 1954)
-

the systems $\text{BaTiO}_3\text{-SrTiO}_3$ and $\text{CaTiO}_3\text{-SrTiO}_3$ but limited miscibility in the system $\text{CaTiO}_3\text{-BaTiO}_3$ (Kwestroo and Paping, 1959).

OCCURRENCE

The occurrence of perovskite (except nearly Ca-free varieties) is restricted to rocks which are markedly undersaturated with silica such as carbonatites, ultramafics, phonolites, basic pegmatites and metamorphosed limestones. Mineral associations of perovskite are given in Table 37. Perovskite cannot stably coexist with minerals such as quartz, enstatite (a pyroxene, MgSiO_3) and alkali feldspars ($(\text{Na,K})\text{AlSi}_3\text{O}_8$) (Schuiling and Vink, 1967). In the presence of H_2O perovskite reacts with these phases at 700°C and 1 Kbar according to the following equations:

The association of perovskite with silica, feldspars and enstatite is unstable at lower temperatures as well (Schuiling and Vink, 1967). Hence the nonoccurrence of perovskite in granites, syenites and many basalts. In the absence of H_2O or at low temperatures kinetics of perovskite + "silica" reactions are probably sluggish. Loparite and irinite differ from perovskite in their mode of occurrence since they are stable with alkali feldspars. Loparite and irinite are found in syenite and nepheline syenite. Loparite has been reported as a placer mineral (Gurivich, et al., 1960). Perovskite varieties older than 5×10^8 years BP are known (Semenev and Shuba, 1959).

ALTERATION

At high temperatures, perovskite of a composition near CaTiO_3 will alter toward titanite (CaTiSiO_5) if it is exposed to solutions in contact with saturated silicates such as enstatite, alkali feldspars

Table 37: Minerals Associated with Perovskite (after Smith, 1970).

	1	2	3	4	5	6	7	8
Magnetite (Fe_3O_4)	X	X	X	X	X	X	X	X
Ilmenite (FeTiO_3)				X				
Spinel (MgAl_2O_4)	X	X						
Sphene (CaTiSiO_5)						X	X	X
Olivine ($(\text{Mg,Fe})_2\text{SiO}_4$)	X	X		X	X			
Monticellite (CaMgSiO_4)	X							
Pyroxene ($\text{A}_2^{+2}\text{Si}_2\text{O}_6$)			X	X	X	X	X	X
Phlogopite ($\text{K}_2(\text{Mg,Fe})_6\text{Si}_6\text{Al}_2\text{O}_{20}(\text{OH,F})_4$)	X		X	X	X			
Nepheline (NaAlSiO_4)			X	X	X	X	X	X
Kalsilite (KAlSiO_4)			X		X			
Leucite (KAlSi_2O_6)				X		X	X	X
Melilite ($(\text{Ca,Na})_2(\text{Mg,Fe,Al,Si})_3\text{O}_7$)		X	X					

-
1. Monticellite peridotite, Haystack Butte, Montana
 2. Melilitite, Dwinberg (near Wortenberg) Czechoslovakia
 3. Melilite-nephelinite, inner wall of upper crater, Nyiragongo, Congo
 4. Ugandite, Katwe volcanic field, Uganda
 5. Mafurite, Katwe volcanic field, Uganda
 6. Nephelinite, Mt. Etinde, W. Africa
-

and quartz. Niobian perovskite with alteration rims of pyrochlore $((\text{Na}, \text{Ca}, \text{REE}, \text{U})_2(\text{Nb}, \text{Ta}, \text{Ti})_2\text{O}_6(\text{O}, \text{OH}, \text{F}))$ have been reported by Nickel and McAdam (1963). Loparite has been reported to alter to "rare earth oxides of the pyrochlore type" (Gorzhevskaya and Sidorenko, 1969), pseudomorphs of "hydropyrochlore" (Semenev *et al.*, 1963) and to monazite and anatase (TiO_2) (Kalenov, *et al.*, 1963). In a nepheline syenite pegmatite veined by albite, irinite has been locally replaced by albite (Borodin and Kazakova, 1954). In a metasomatized pyroxenite, perovskite with reaction rims of ilmenite (FeTiO_3) and anatase have been observed (Lebedev and Rinskaya-Korsakova, 1949). During talc alteration of a serpentized kimberlite, perovskite has been replaced by leucoxene (an ill defined mixture of titanates) (Susov, 1962). Alteration of serpentine to talc implies temperatures of 800°C or less. Most of these alteration effects are attributed to metasomatism (corrosion by hydrothermal solutions) rather than surface weathering.

RADIATION DAMAGE

The perovskite structure is susceptible to radiation damage or metamictization. Iritite and loparite with 3 to 13 wt% ThO_2 occur as a metamict mineral (Borodin and Kazakova, 1954; Gorzhevskaya and Sidorenko, 1969). Perovskite containing less than 0.2 wt% $(\text{Th}, \text{U})\text{O}_2$ show broadening of x-ray diffraction maxima. When these slightly damaged perovskites are annealed at 1000°C for 5-6 hours, the diffraction maxima sharpen and the density increases by 0.5 - 0.7% (Frank-Kamenetskii and Vesel'skii, 1961).

$^{244}\text{CmAlO}_3$ (polycrystalline) is a synthetic compound with the perovskite structure which becomes x-ray amorphous within about eight days after preparation. The theoretical density of CmAlO_3 decreases by about 6.5% before it becomes amorphous to x-rays (Mosley, 1971). Table 38 is a list of radiation damage effects which may be observed in perovskite as a function of time, radioactive isotope and wt% of selected alpha emitters. This data is extrapolated

Table 38: Radiation Damage effects in perovskite from small amounts of TRU elements. Extrapolated from data on CmAlO_3 (Mosley, 1971). Contributions from radioactive daughters has been ignored. It has been assumed that both CaTiO_3 and CmAlO_3 become x-ray amorphous after a dose of 5.04×10^{20} alpha disintegrations per gfw.

Isotope	Wt %	Halflife	Years required to become	
			"50% metamict" ($\Delta v/v = 3.3\%$)	"10% metamict" ($\Delta v/v = 0.65\%$)
^{244}Cm	0.10	18.1 yrs.	36 yrs.	4.3 yrs.
^{244}Cm	0.02	18.1	(a)	36
^{238}Pu	0.10	89	178	21.2
^{238}Pu	0.02	89	(a)	178
^{239}Pu	0.10	24500	49000	5900
^{239}Pu	0.02	24500	(a)	49000

(a) Decay of radioactive daughter isotopes would be necessary to achieve this degree of radiation damage. Of the isotopes listed only ^{244}Cm decays to a short lived isotope (^{240}Pu , $t_{1/2} = 6580$ years).

from data on $^{244}\text{CmAlO}_3$; thus it is at best an approximation of radiation damage effects which may be observed in SYNROC-perovskite.

PEROVSKITE

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ZIRCONOLITE: $\text{CaZrTi}_2\text{O}_7$

Zirconolite is an analogue for the SYNROC zirconolite phase, $(\text{Ca}, \text{Zr}, \text{U}, \text{REE}, \text{TRU})_2\text{Ti}_2\text{O}_7$. The zirconolite structure is derived from the pyrochlore, $\text{NaCaNb}_2\text{O}_6\text{F}$, structure. The mineral is subject to radiation damage but is otherwise durable. Zirconolite occurs in silica undersaturated rocks and placer deposits.

MINERAL DATA

Mineral data for zirconolite are as follows:

Formula: $\text{CaZrTi}_2\text{O}_7$ (ideal) or $(\text{Ca}, \text{Zr}, \text{REE}, \text{U}, \text{Th})_2(\text{Ti}, \text{Nb})_2\text{O}_7$

Crystal System:	Monoclinic
Z:	8
Lattice Constants:	$a = 12.43$ $b = 7.26$ $c = 11.35\text{\AA}$ $\beta = 100.57^\circ$
Mohs Hardness:	5.5 - 6.0
Density (gm/cm^3):	4.0 - 4.5

STRUCTURE

Zirconolite ($\text{CaZrTi}_2\text{O}_7$) has a distorted pyrochlore structure. In zirconolite Ca and Zr are coordinated by approximate cubes of eight oxygens while Ti is coordinated by six oxygens. Figure 30 is a representation of the pyrochlore ($\text{NaCaNb}_2\text{O}_6\text{F}$) structure. In pyrochlore, Na, Ca, REE and U can occupy cubic sites while Nb, Ta and Ti are at the centers of distorted octahedrons of oxygen atoms. Each AO_8 cube shares six edges with other AO_8 cubes and six edges with BO_6 octahedra. Each BO_6 octahedron shares six edges with AO_8 cubes and two corners with other BO_6 octahedra (Pyatenko, 1960). The pyrochlore structure is derived from the UO_2 structure by systematically deleting one-eighth of the oxygen atoms. This converts one-half of the occupied cubic sites to octahedrons, doubles the unit cell edge and lowers the symmetry from Fm3m to Fd3m. Crystallographic data for zirconolite, pyrochlore and related compounds are given in Table 39.

CHEMISTRY

Compositions for some zirconolites are given in Table 40. Up to 10 wt% $(\text{U}+\text{Th})\text{O}_2$ can be present though 5 wt% is more typical. Lunar zirconolite can have 16 wt% REE_2O_3 but terrestrial zirconolite tends to have 6 wt% REE_2O_3 or less. Nb_2O_5 content approaches 25 wt% in niobian zirconolite (Borodin, et al., 1960). SrO does not occur in significant amounts in zirconolite. $\text{FeO}+\text{Fe}_2\text{O}_3$ are present in amounts of 5 - 7 wt%. Hydration of the mineral accompanies metamictization. Vlasov (1964) indicates that alteration increases the SiO_2 content.

OCCURRENCE

Zirconolite is a rare mineral that has not received large amounts of attention. Zirconolite occurs in pyroxenities, carbonatites and in placer material derived from these rocks (Vlasov, 1964). Zirconolite over 2×10^9 years BP has been reported from placer deposits on Ceylon

Figure 30. Polyhedral representation of the pyrochlore structure (Pyatenko, 1960).

Table 39: Crystallographic Data for Zirconolite and Pyrochlore Type Phases.

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	System/S.G.	a(A)	b(A)	c(A)	B(°)	³ V(A)	Z	(gm/cm ³)
1. CaZrTi ₂ O ₇	monoclinic	12.43	7.26	11.35	100.57	1006.9	8	
2. CaZrTi ₂ O ₇ (metamict zirconolite roasted at 800°C)	cubic/Fm3m?	5.02	-	-	-	126.5	1	-
3. Gd ₂ Ti ₂ O ₇	cubic/Fd3m	10.186	-	-	-	1056.8	8	6.705
4. La ₂ Ti ₂ O ₇	monoclinic/P2 ₁ or P2 ₁ /m	13.015	5.5456	7.817	98.64	557.8	4	5.782
5. Y ₂ Ti ₂ O ₇	cubic/Fd3m	10.09	-	-	-	1027.2	8	4.99
6. Pyrochlore (NaCaNb ₂ O ₆ F)	cubic/Fd3m	10.3 - 10.4	-	-	-	1108	8	-

JCPDS Powder Diffraction File Number or Reference:

1. 17 - 495	4. 28 - 517 (distorted pyrochlore structure)
2. 15 - 12	5. 27 - 982 (pyrochlore structure)
3. 23 - 259 (pyrochlore structure)	6. Frondel, 1958

Table 40: Chemical analysis of Zirconolite.

	1.	2.	3.	4.	5.	6.
Na ₂ O	-	0.37	1.40	-	-	0.46
K ₂ O	0.24	-	-	-	-	-
CaO	12.03	11.05	11.00	8.55	4.6	10.79
MgO	0.5	0.45	-	1.33	0.58	0.50
MnO	0.12	0.06	0.38	-	-	0.13
FeO	2.85	-	6.00	4.72	-	0.36
Fe ₂ O ₃	3.44	5.49	1.11	-	6.5	4.60
Al ₂ O ₃	2.23	1.03	-	-	1.14	1.04
REE ₂ O ₃	3.36	6.22	4.00	0.32	16.24	6.00
SiO ₂	1.18	2.05	-	-	1.08	4.50
TiO ₂	32.25	31.69	18.19	36.26	26.9	29.91
ZrO ₂	35.75	32.84	25.00	34.19	40.7	31.17
ThO ₂	0.37	0.58	2.90	8.33	0.46	0.46
U ₃ O ₈	0.10	1.53	0.40	4.66	0.21(UO ₂)	1.75
Nb ₂ O ₅	4.25	3.26	24.84	-	0.40	2.86
Ta ₂ O ₅	0.09	-	2.00	-	-	-
H ₂ O ⁻	0.09	3.35	2.48	1.70	-	5.66
H ₂ O ⁺	1.56	-	-	-	-	-
F	-	-	0.60	-	-	-
PbO	-	-	-	-	0.23	-
HfO ₂	-	-	-	-	0.47	-
Total	100.44	99.97	100.30	100.06	99.95	100.19

1. Dark zirconolite, Aldan, U.S.S.R. (Vlasov, 1966)
 2. Brown zirconolite, Kola Peninsula, U.S.S.R. (Vlasov, 1966)
 3. Niobian zirconolite, Kola Peninsula (Vlasov, 1960)
 4. "Zirkelite" from Ceylon (Vlasov, 1966)
 5. Lunar zirconolite, Apollo 12 (Busche, et al., 1972)
 6. Light brown zirconolite, Kola (Vlasov, 1966)
 The ideal composition of zirconolite is CaO, 16.54%, ZrO₂, 36.33%; TiO₂, 47.13%.

(Pudovkina et al., 1974). Minerals with which zirconolite is known to occur include nepheline, perovskite, titanite (CaTiSiO_5), magnetite, pyroxenes, apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F})$), pyrochlore, $((\text{Ca}, \text{Na})_2 - (\text{Nb}, \text{Ta})_2\text{O}_7)$, baddeleyite (ZrO_2), calcite, dolomite ($\text{CaMg}(\text{CO}_3)_2$), amphiboles, and phlogopite (Vlasov, 1966; Bulakh, et al., 1960; Borodin, et al., 1956; Borodin, et al., 1960). Lunar zirconolite occurs with calcic plagioclase $((\text{Ca}, \text{Na})\text{Al}(\text{Al}, \text{Si})\text{Si}_2\text{O}_8)$ (Busche, et al., 1972), though no mention is made of terrestrial zirconolite occurring with feldspars. In granite and syenite rocks, zircon and other zirconium silicate minerals appear to occur in place of zirconolite.

ALTERATION AND RADIATION DAMAGE

Alteration of zirconolite is not frequently mentioned, in fact any mention of zirconolite in mineralogic literature is rare. Vlasov (1964) indicates that alteration increases the contents of H_2O and SiO_2 . Areas along micro-fractures in most zirconolites show compositional changes, much of it due to hydration. The mineral may be quite durable as zirconolite over 2×10^9 years old has been found in placer gravel in Ceylon (Pudovkina, et al., 1974).

Pyrochlore and zirconolite are susceptible to metamictization. Varieties of zirconolite with as little as 1.58 wt% U_3O_8 + 0.58 wt% ThO_2 are metamict (Borodin, et al., 1956). Vlasov reports a partially metamict zirconolite with a density of 4.37 and a metamict zirconolite with a density of 4.02, a density difference of at least 8.0%. When partially or completely metamict zirconolite is annealed at $650\text{--}800^\circ$, a metastable fluorite type phase is obtained. Above 1100°C , the original structure is regained (Borodin, et al., 1960; Bulakh, et al., 1960).

ZIRCONOLITE

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DISCUSSION AND CONCLUSIONS

The main processes which will affect a waste form can be divided into two groups: (1) chemical alteration and (2) radiation effects. Chemical alteration includes corrosion and leaching. Possible radiation effects include radiation damage from alpha emitters and phase instability arising from transmutation of fission products (Cs and Sr).

CHEMICAL ALTERATION

One indication of the durability of minerals is their ability to survive weathering and become concentrated in secondary environments such as old sand or gravel deposits. On this basis natural analogues can be described as durable, durable under reducing conditions or not durable. The limitation of this classification scheme is that it assumes surface disposal under oxidizing conditions at low temperatures. Using this durability criteria, natural analogues to SYNROC and supercalcine are classified in Table 41.

Considering supercalcine phases first, pollucite is unstable under surface conditions and its stability field is not well defined. If pollucite is unstable under waste repository conditions, Cs loss becomes a problem as soon as water is in contact with the primary waste form. Loss of Cs from pollucite could proceed rapidly. At low temperatures, pollucite can alter to clays or other zeolites with loss of Cs. Nepheline appears to be unstable at temperatures below 400–500°C, at moderate to high pressures in the presence of water. Numerous zeolites are listed as alteration products of nepheline. Nepheline will react with SiO_2 (and hence granitic rocks) at high temperatures.

Estimates of the durability of the scheelite phase, SrMoO_4 are difficult to make from natural analogues. SrMoO_4 has not been reported as a mineral, and powellite, CaMoO_4 , is uncommon. CaMoO_4 and SrMoO_4 may not be as durable as scheelite (CaWO_4).

Table 41: Durability of natural analogues to SYNROC and supercalcline phases. Criteria and qualifications listed in the text should be noted.

Mineral	Durable	Durable(reducing conditions only)	Not durable
Baddeleyite, ZrO_2	X	-	-
Nepheline, NaAlSiO_4	-	-	X
Pollucite, $\text{CsAlSi}_2\text{O}_6$	-	-	X
Scheelite Ca(W,Mo)O_4	X	-	-
Sodalite, $\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{Cl}_2$	-	-	X
Apatite, $(\text{Ca,REE})_5(\text{SiO}_4)_3\text{OH}$	X ¹	-	-
Monazite, $(\text{Ce,L a})\text{PO}_4$	X ¹	-	-
Uraninite, UO_2	-	X	-
Priderite ² , $(\text{K,Ba})_{2-x}(\text{Fe,Ti})_8\text{O}_{16}$	rare occurrence, possibly quite durable		
Perovskite ² , $(\text{Ca,REE})_{1-x}\text{TiO}_3$	X	-	-
Zirconolite ² , $\text{CaZrTi}_2\text{O}_7$	X	-	-

1. Ce in these minerals is subject to oxidation

2. SYNROC phases

The solubility of the spinel phase is quite low. Unless reducing conditions and high pH prevail in the waste repository, magnetite (Fe_3O_4) would alter to hematite (Fe_2O_3). Trevorite (NiFe_2O_4) is too uncommon to allow any predictions. Chromite (FeCr_2O_4) frequently develops alteration rinds, but no consistent alteration pattern is apparent other than loss of Mg and Al.

Monazite and apatite should be stable phases although the Ce^{+3} can be oxidized. The stability of the uraninite phase ($(\text{U,Ce,Zr})\text{O}_2$) is uncertain. It would be quite stable and insoluble under reducing conditions, but will be subject dissolution in an oxidizing environment. Natural baddeleyite (ZrO_2) is quite stable, although it will react with SiO_2 (and hence granitic rocks) at high temperatures.

The durability of SYNROC zirconolite and perovskite may be excellent. Zirconolite appears to be durable. The main chemical alteration effects reported for zirconolite are, hydration and increased SiO_2 content; however, zirconolite is not a common mineral. Zirconolite, perovskite and "hollandite" are thermodynamically unstable with high-silica rocks. This may not be important at low temperatures or in the absence of H_2O . Perovskite is more common than zirconolite, and the mineral has been thoroughly studied. There are numerous alteration products of perovskite though some of the alteration processes may have occurred at elevated temperatures. "Hollandite" does not have a close natural analogue. Priderite, $\text{K}_2\text{Fe}_2\text{Ti}_6\text{O}_{16}$ (with minor Ba and Al), is supposed to be isostructural with "hollandite", $\text{BaAl}_2\text{Ti}_6\text{O}_{16}$, but it is a poor compositional analogue. Priderite is extremely rare.

RADIATION EFFECTS

The waste form will be exposed to alpha, beta and gamma radiation. Alpha decay is the only radioactive disintegration process which produces heavy, highly energetic particles. It is thus the only decay process which will be able to displace large numbers of atoms from their sites in crystalline actinide phases. Most actinide

crystalline phases are susceptible to damage by alpha particles and recoil nuclei. It is notable that the monazite and UO_2 structures appear to be highly resistant to radiation effects. The apatite, perovskite and zirconolite structures are susceptible to alpha radiation damage and may become metamict. Metamict, natural apatite, perovskite and zirconolite have glass-like physical properties, decreased density and show enhanced hydration effects.

The term transmutation is often applied to the beta decay of $^{137}\text{Cs}^+$ to $^{137}\text{Ba}^{+2}$ and $^{90}\text{Sr}^{+2}$ to $^{90}\text{Zr}^{+4}$.

The beta particles and their recoil nuclei are ineffective at displacing atoms, but changes in ionic radius and charge may have a destabilizing effect on the scheelite, pollucite and hollandite structures. Using pollucite and hollandite as examples, it can be assumed that small amounts of Ba can substitute for Cs. As ^{137}Cs decays to ^{137}Ba the following may occur:

1. Ba could "inherit" the +1 oxidation state from ^{137}Cs and there would be no charge compensation problem. This is unlikely since there are no known stable Ba^{+1} compounds.
2. Ba would be reduced to Ba metal, or the framework cations (Si, Ti, Al) would be reduced to maintain charge balance.
3. Cations (Ba or Cs) would be leached from the structure.
4. The Al/Si or Al/Ti ratio would change,
5. Additional anions would be taken into the structure.

The effects of transmutation and metamictization are being evaluated at PNL and elsewhere. In general, radiation effects will be more pronounced at higher waste loadings.

RECOMMENDATIONS

1. The stabilities of all supercalcine and SYNROC phases under the anticipated waste repository conditions (temperature, pressure, Eh, pH, ionic strength and trace element presence) must, of course, be determined.
2. The affects of α -radiation damage on the integrity of actinide bearing supercalcine and SYNROC phases must be evaluated since transuranium elements are present in quantities of about .1 - .2 mole % in the waste stream.
3. The affects of transmutation of Cs to Ba and Sr to Zr on the integrity of the pollucite, scheelite, apatite, perovskite and hollandite should be further investigated.
4. In the event α -radiation damage or transmutation are shown to pose serious problems for crystalline waste forms, then serious consideration should be given to reduced waste loadings.
5. Much of the uranium in igneous rocks occurs as thin films on grains. Any crystalline waste form must avoid this as much as possible.
6. Alternatives to pollucite as a cesium bearing phase should be investigated. Regardless of the host phase, loss of Cs is likely to be a problem if the primary waste form comes into contact with water.

GLOSSARY

The following glossary provides definitions for the geologic and mineralogic terms used in this report. Most of the definitions have been adopted from the Glossary of Geology (published by the American Geological Institute), although a few of the mineralogic definitions have been taken from the 1975 Glossary of Mineral Species (by Michael Fleisher, published by Mineralogical Record, Inc.)

AEGIRINE - A series of monoclinic pyroxene minerals $(\text{Na,Ca})-(\text{Mg,Fe})\text{Si}_2\text{O}_6$.

ALBITE - A triclinic rock forming mineral, $\text{NaAlSi}_3\text{O}_8$, of the feldspar group.

ALKALIC ROCK - Igneous rock with a high alkali content.

AMPHIBOLE - A rock forming mineral group having the general formula $\text{A}_{2-3}\text{B}_5(\text{Si,Al})_4\text{O}_{11}(\text{OH})_2$, $\text{A} = \text{Fe}^{+2}, \text{Ca}, \text{Na}$ and $\text{B} = \text{Fe}^{+2}, \text{Fe}^{+3}$ and Al .

AMPHIBOLITE FACIES - Medium grade metamorphism characterized by hornblende and plagioclase of composition An_{17} .

AMYGDULE - A gas cavity in an igneous rock which is filled by secondary minerals.

ANORTHOSITE - A plutonic rock composed almost entirely of plagioclase.

APLITE - A light colored, fine-grained dike rock whose composition may range from granitic to gabbroic.

AUGITE - A pyroxene mineral, $((\text{Ca,Na})(\text{Mg,Fe,Al})(\text{Si,Al})_2\text{O}_6)$.

AUTHIGENIC - Said of a rock or rock component which was generated in situ instead of being transported.

BASALT - A dark igneous rock composed primarily of calcic plagioclase, pyroxene and sometimes olivine.

BASIC - Said of an igneous rock which has relatively low silica contents, 45-52% SiO_2 .

BATHOLITH - A large body of intrusive igneous rock.

BEDROCK - Any solid rock which underlies gravel, clay or soil.

BERYL - A hexagonal mineral, $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$, occurring mainly in granitic pegmatites.

BIOTITE - A monoclinic mineral of the mica group, $\text{K}(\text{Mg,Fe}^{+2})_3-(\text{Al,Fe}^{+3})\text{Si}_3\text{O}_{10}(\text{OH})_2$.

BOEHMITE - A mineral, $\text{AlO}(\text{OH})$, which is an orthorhombic dimorph of diaspore.

CANCRINITE - A hexagonal mineral with the approximate formula: $\text{Na}_3\text{Ca}(\text{AlSiO}_4)_3\text{CO}_3$.

CARBONATITE - An igneous or metamorphic rock composed mostly of carbonate minerals.

CASSITERITE - Tetragonal SnO_2 .

CHLORITE - A monoclinic group of hydrous silicates of aluminum, ferrous iron and magnesium which are closely related to the micas. Common in low grade metamorphic rocks.

CHLORITIZATION - Replacement by conversion to, or introduction of chlorite.

CHROMATITE - A tetragonal mineral, CaCrO_4 .

CHURCHITE - A monoclinic mineral, $\text{YPO}_4 \cdot 2\text{H}_2\text{O}$.

COLLOFORM - Rounded masses of mineral which result from colloidal precipitation.

CRYPTOCRYSTALLINE - Crystalline, but individual crystallites cannot be distinguished with a magnifying lens.

DETRITAL - Minerals occurring in sedimentary rocks which were derived from previous rocks.

DEUTERIC - A term applied to alteration in an igneous rock produced during the last stages of, and as a consequence of, the consolidation of magma or lava.

DIAGENESIS - The chemical and physical changes that sediments undergo before being consolidated into a sedimentary rock.

DIASPORE - An orthorhombic mineral, AlO(OH) , which is dimorphic with boehmite.

DIORITE - A plutonic igneous rock composed essentially of Na-plagioclase, hornblende, biotite or pyroxene.

DRUSE - A rock cavity lined with crystals.

DUNITE - A rock consisting of olivine with enstatite (MgSiO_3) and chrome spinel.

ELUVIAL - A term applied to deposits formed by the decomposition of rock in situ.

EPITHERMAL - Ore deposits formed in and along fissures and cavities in rocks by deposition near the surface from ascending hydrothermal solutions.

EXSOLVE - The formation of two phases from one solid solution phase.
FACIES - A group of rocks characterized by a definite set of minerals formed under particular metamorphic conditions. The composition and proportion of mineral phases in the rocks of a given facies vary gradually in correspondence with variation in the chemical composition of the rocks.

FELDSPAR GROUP - A group of triclinic and monoclinic rock forming minerals, $(\text{Na}, \text{K}, \text{Ba}, \text{Ca})(\text{Al}, \text{Si})\text{AlSi}_2\text{O}_8$.

FELDSPATHOID - Minerals similar to feldspars but with less SiO_2 . Examples are zeolites and nepheline.

FELSIC - Light colored igneous rocks containing feldspars or feldspathoids.

FELSITE - An igneous rock with or without large crystals, which consists of cryptocrystalline aggregates of felsic minerals, particularly quartz and K-feldspar.

FOYAITE - Synonymous with nepheline syenite.

GABBRO - A plutonic rock consisting largely of calcic plagioclase and clinopyroxene.

GABBRO CLAN - The group of igneous rocks which includes gabbros, diabases and basalts. The chief mineral constituents of gabbros in order of abundance are calcic plagioclase, augite, hypersthene and olivine.

GARNET - A cubic rock-forming mineral having the general formula $\text{A}_3\text{B}_2(\text{SiO}_4)_3$. A = Mg, Fe, Mn, Ca and B = Al, Fe, Ti, Cr.

GIBBSITE - Monoclinic $\text{Al}(\text{OH})_3$.

GISMONDINE - A monoclinic zeolite group mineral, $\text{Ca}(\text{Al}_2\text{Si}_2)\text{O}_8\cdot 4\text{H}_2\text{O}$.

GLAUCOPHANE - An amphibole mineral, $\text{Na}_2(\text{Mg}, \text{Fe})_3\text{Al}_2\text{Si}_8\text{O}_{22}(\text{OH})_2$.

GNEISS - A coarse-grained rock in which bands of granular minerals alternate with bands of schistose minerals.

GOETHITE - An orthorhombic mineral, $\text{FeO}(\text{OH})$.

GRANITE - A rock consisting of K-feldspar, quartz and mica.

GRANODIORITE - A plutonic igneous rock consisting of quartz, calcic oligoclase and orthoclase with biotite, hornblende or pyroxene as mafic constituents.

GRANULITE - A metamorphic rock belonging to a high temperature group characterized by the presence of mica and hornblende.

GREISEN - A pneumolytically altered granitic rock composed of quartz, mica and topaz.

GREENSCHIST - A metamorphosed basic igneous rock containing major amounts of chlorite.

HORNBLENDE - An amphibole group mineral, monoclinic $(\text{Ca,Na})_{2-3}(\text{Mg,Fe,Al})_5(\text{Al,Si})_8\text{O}_{22}(\text{OH})_2$.

HYDROTHERMAL - A term applied to hot fluids rich in water, and to rocks, ore deposits and alteration products produced by them.

HYPABYSSAL ROCKS - Minor intrusions of igneous rocks which have risen towards but failed to reach the surface.

HYPOTHERMAL - Said of a rock or deposit which originated at relatively high temperatures (300-500°C).

ILLITE - A group of clay minerals, intermediate in composition between muscovite and montmorillonite, which are common in clay containing sedimentary rocks.

ILMENITE - A hexagonal mineral, FeTiO_3 .

ISOMORPHOUS - Said of two phases with different compositions but the same structure.

ISOSTRUCTURAL - Isomorphous.

JASPER - Impure, slightly translucent cryptocrystalline quartz.

JASPILITE - A rock consisting of alternating bands of jasper and iron oxides.

KAOLINITE - A common clay mineral, $\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$.

KAOLINIZATION - The replacement of minerals by or alteration of minerals to kaolin.

KIMBERLITE - A variety of mica-containing plutonic igneous rocks consisting essentially of olivine and phlogopite. Kimberlite is silica undersaturated and contains no quartz or alkali-feldspar.

LEPIDOLITE - A monoclinic mineral of the mica group, $\text{K}(\text{Mg,Li,Al})_3(\text{AlSi}_3)\text{O}_{10}(\text{OH,F})_2$.

LEUCITE - A pseudo-cubic mineral found in low SiO_2 , K-rich volcanic rocks, KAlSi_2O_6 .

MAFIC - Said of basic rocks which are composed primarily of Mg-silicate minerals.

MAGHEMITE - A cubic, cation-deficient spinel which is dimorphous with hematite.

MARTITE - Ferric oxide, Fe_2O_3 , which occurs as pseudomorphs after magnetite.

MELANITE - A black variety of andradite garnet, $\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_3$.

MELILITE - A group of tetragonal minerals, $(\text{Na,Ca})_2(\text{Mg,Al})-(\text{Al,Si})_2\text{O}_7$. Also a rock composed of melilite, olivine and augite.

MESOTHERMAL - Said of ores which were deposited at intermediate temperatures and depths.

METASOMATIC - Synonym for "replacement". Said of a phase which is a hydrothermal corrosion product of pre-existing rocks or the result of cation exchange.

METAMICT - Radioactive minerals which were once crystalline but due to radiation damage are now amorphous to x-rays. Metamictization is accompanied by hydration, reduced density and refractive index.

MIGMATITE - A composite rock produced by partial melting.

MONTICELLITE - An orthorhombic mineral, CaMgSiO_4 , which sometimes occurs in metamorphosed limestone.

MONTMORILLONITE - A group of clay minerals.

MONZONITE - A granular plutonic rock containing approximately equal amounts of orthoclase and plagioclase.

MUSCOVITE - A monoclinic mineral of the mica group, $\text{KAl}_2(\text{Si}_3\text{Al})-\text{O}_{10}(\text{OH})_2$.

NATROLITE - An orthorhombic zeolite mineral, $\text{Na}_2\text{Al}(\text{AlSi})_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$.

NEPHELINE SYENITE - An undersaturated plutonic rock composed of alkali feldspars, nepheline feldspathoids and one or more mafic minerals. Primary silica minerals are absent.

OLIGOCLASE - A triclinic feldspar, $(\text{Na,Ca})(\text{Al,Si})\text{AlSi}_2\text{O}_8$.

OLIVINE - An orthorhombic mineral, $(\text{Mg,Fe})_2\text{SiO}_4$, which is common in basic and ultra-basic rocks.

ORTHOPYROXENE - A pyroxene group mineral.

PARAGONITE - A monoclinic mineral of the mica group, $\text{NaAl}_2(\text{AlSi})_3\text{O}_{10}(\text{OH})_2$.

PEGMATITE - Intrusive, igneous rock bodies, consisting of large crystals, usually of granitic composition.

PELITIC SCHIST - A schist derived from a pelite. Pelites consist of clay minerals (illite, montmorillonite, kaolinite), chlorite, detrital muscovite, occasional feldspar and quartz which is a major constituent.

PERIDOTITE - An ultramafic (low silica) rock composed of pyroxene and olivine.

PERRIERITE - A monoclinic mineral, $(\text{Ca,Ce,Th})_4(\text{Mg,Fe})_2(\text{Ti,Fe}^{+3})_3\text{Si}_4\text{O}_{22}$, which is dimorphous with chevkinite.

PHONOLITE - Extrusive equivalent of a nepheline syenite. Principal components are soda orthoclase, nepheline and aegirine-diopside.

PIGEONITE - A monoclinic pyroxene, $\text{Mg}(\text{Mg,Ca})(\text{SiO}_3)_2$.

PLACER DEPOSIT - A mass of sand or gravel which resulted from the erosion of rock and which contains durable minerals such as gold, monazite, zircon, garnet and magnetite.

PLAGIOCLASE - A triclinic feldspar, $(\text{Ca,Na})\text{Al}(\text{Si,Al})\text{Si}_2\text{O}_8$.

PLEONASTE - A variety of spinel, $(\text{Mg,Fe})(\text{Al,Fe})_2\text{O}_4$.

PLUTON - A body of rock formed beneath the surface of the earth by consolidation of a magma.

POLYMORPHS - Said of phases which have the same composition but different structures.

PORPHYRITIC - Said of a fine-grained rock which also contains large crystals.

PSEUDOBROOKITE - An orthorhombic mineral, Fe_2TiO_5 .

PSEUDOMORPH - A crystal or apparent crystal which has the external morphology of a mineral which has been replaced by substitution or by chemical alteration.

PYRITE - A cubic mineral, FeS_2 .

PYROCLASTIC - Detrital volcanic materials that have been explosively ejected from a volcanic vent.

PYROPHYLLITE - An orthorhombic mineral, $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$.

PYROXENE - A group of orthorhombic triclinic and monoclinic rock forming minerals, RSiO_3 , $\text{R}=\text{Ca}, \text{Mg}, \text{Fe}, \text{Mn}, \text{Zn}$.

PYROXENITE - A low silica rock composed of enstatite (MgSiO_3) or augite ($(\text{Ca},\text{Na})(\text{Mg},\text{Fe},\text{Al})((\text{Al},\text{Si})_2(\text{O}_6))$) or both.

PYRRHOTITE - A hexagonal, magnetic mineral, $\text{Fe}_{n-1}\text{S}_n$, $5 \leq n \leq 16$.

RHYOLITE - The fine-grained equivalent of a granite.

RUTILE - A tetragonal mineral, TiO_2 , which is trimorphous with brookite and anatase.

SANIDINE - Monoclinic KAlSi_3O_8 .

SCHIST - A medium- or coarse-grained metamorphic rock composed primarily of micaceous minerals.

SERICITE - A fine-grained variety of several types of mica.

SERPENTINE - A rock forming mineral, $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$.

SIDERITE - A mineral FeCO_3 sometimes containing Mg or Mn.

SILICA OVERSATURATED - Said of a rock which contains quartz or a primary silica mineral.

SILICA SATURATED - Said of a rock which contains neither quartz nor a feldspathoid.

SILICA UNSATURATED - Said of a rock which contains feldspathoids but no quartz.

SILLIMANITE - An orthorhombic mineral, Al_2SiO_5 , which is trimorphous with kyanite and andalusite.

SKARN - Rocks composed nearly entirely of lime-bearing silicates and derived from nearly pure limestones and dolomites into which Al, Si, Fe and Mg have been introduced.

SMECTITE - A green clay $(\frac{1}{2}\text{Ca},\text{Na})_{0.7}(\text{Al},\text{Mg},\text{Fe})_4[(\text{Si},\text{Al})_8\text{O}_{20}](\text{OH})_4 \cdot n\text{H}_2\text{O}$.

STAUROLITE - An orthorhombic metamorphic mineral, $(\text{Fe},\text{Mg})_2\text{Al}_9\text{Si}_4\text{O}_{23}(\text{OH})$.

SUBFACIES - Minor departures from the standard mineral assemblages within a facies due to small differences in temperature and pressure, but not due to chemical differences.

SUPERGENE - Said of ore deposits which were formed by groundwater.

SYENITE - A plutonic, igneous rock consisting principally of alkali feldspar and one or more mafic minerals such as hornblende or biotite. Either quartz or nepheline are present.

SYNOROGENIC - Said of a process, usually the emplacement of plutons or recrystallization of metamorphic rocks, which occurred at the same time as mountain building.

TALC - A soft mineral, $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$, which is common in metamorphosed mafic rocks.

TACTITE - A rock of complex mineralogical composition which is formed by contact metamorphism or metasomatism of carbonates.

TEKTITE - A high-silica, impact glass.

TEKTOSILICATE - A silicate or aluminosilicate in which all SiO_4 (and AlO_4) tetrahedra share all oxygens with adjacent tetrahedra to build a three dimensional polymeric structure.

TEPHRITE - A volcanic rock composed of calcic plagioclase, titan-augite and nepheline or leucite.

THOMSONITE - An orthorhombic mineral of the zeolite group, $\text{NaCa}_2(\text{AlSi})_5\text{O}_{20} \cdot 6\text{H}_2\text{O}$.

TINGUAITE - A dike rock composed of alkali-feldspar, nepheline, alkalic pyroxene and amphibole. Commonly porphyritic.

TOURMALINE - A hexagonal borosilicate of Na, Li, Mg, Fe and Al which occurs in pegmatites.

TRACHTYTE - The extrusive equivalent of a syenite.

ULTRAMAFIC - Said of a rock which contains no felsic minerals.

ULVOSPINEL - $\text{Ti}^{+4}\text{Fe}_2\text{O}_4$, a cubic spinel mineral.

USSINGITE - A triclinic mineral, $\text{Na}_2\text{AlSi}_3\text{O}_8(\text{OH})$.

UVAROVITE - A garnet, $\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3$.

WALL ROCK - The country rock which forms the walls of a vein or surrounds a pluton.

WOLLASTONITE - A triclinic mineral, CaSiO_3 .

WOLFRAMITE - A monoclinic mineral, CaWO_4 , which is dimorphous with scheelite.

ZEOLITE - A group of hydrous alumino-silicate minerals of Na, K, Ca, Ba and Sr. Zeolites have open structures, low densities and unusual ion exchange properties.

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Idaho Falls, ID 83401

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