Fractional Differentiation of Silicate Minerals during Oil Shale Processing: A Tool for the Prediction of Retort Temperatures

Glenn M. Mason

Department of Geosciences, Indiana University Southeast
New Albany, Indiana 47150
gmason@ius.edu

Abstract

Bowen's reaction series is a sequence by which igneous minerals crystallize from cooling magmas. Conceived to differentiate natural magmas, mineralogical similarities exist between Bowen's reaction series and the minerals that form during the high temperature processing of oil shale. The mineral suites created high temperature processing of oil shale, although differing from natural magmas by the presence of excess calcium, contain important parallels to their natural counterparts and are both byproducts of the polymerization of the silica tetrahedra. Oil shale processing forms the reaction series monticellite Ψ akermanite-gehlenite Ψ augite-diopside Ψ actinolite-tremolite Ψ clintonite, a Ca-analog to biotite. Using silicate structure equivalents and the resultant temperature regimes that produced the minerals, a modified oil shale reaction series, modeled after Bowen=s Reaction Series, can serve as a tool to interpret minerals and temperatures generated during oil shale processing.

Introduction and Background

The concept of fractional crystal differentiation was proposed by N. L. Bowen from the study of basaltic magmas (Bowen, 1928). Bowen's reaction series is the sequence by which minerals crystallize from a cooling magma. Basaltic magma is the source of bedrock of the ocean floors, and therefore the most important type of magma on earth. Bowen held the view that all magma was derived from basalt; his reaction series was designed to demonstrate that idea. Although the concept that all magma was derived from basaltic magma is no longer generally accepted, the validity of the reaction series itself has been experimentally proven valid beyond a reasonable doubt.

Similarities exist between the mineral suite formed under conditions of high temperature oil shale processing and Bowen's reaction series. This work presents new insight into the silicate minerals generated when Ca-rich Green River Formation oil shale (kerogenaceous marlstone) is processed at high temperature. Using an excepted and experimentally proven idea, Bowen's reaction series, the concept of fractional crystallization can be applied to the silicate minerals generated during oil shale processing.

The mineral suite created by processing Green River Formation oil shale is significantly influenced by the mineral assemblage of the raw or unprocessed oil shale. It has been well documented that in the stratigraphic zones which contain the greatest abundance of kerogenaceous material in the Green River Formation are rich in the carbonate minerals, especially calcite and minerals of the dolomite family (Smith and Robb, 1966). Silicate minerals, quartz, feldspars, analcime, and clay minerals vary in abundance throughout the formation. As the raw oil shale is pyrolized, two primary mineral reactions can be recognized. First, carbonate minerals decompose releasing Ca, Mg, and Fe, with a corresponding re-

lease of CO_2; and secondly, silicate minerals decompose releasing Si, Al, O, Na, Ca, and K. Due to the mineralogical composition of the original oil shale, the resulting molten material, although compositionally similar to natural rhyolitic magmas, differs significantly due to abundant Ca present. As a consequence, the mineral suite which forms during the processing of Green River Formation oil shale is strongly biased toward Ca-analogs of the minerals that are normally associated Bowen's reaction series.

Experimental

In this study, samples were collected from three different sample sources and processed by three different oil shale technologies. Although, differing with respect to geographic localities, all samples represent materials from the mahogany zone of the Parachute Creek Member of the Green River Formation. Remarkable stratigraphic continuity has been demonstrated for the Green River Formation (Trudell et al., 1970). Minor variations in the initial mineralogical composition of raw oil shale appeared to play no role in influencing the mineral reaction series observed.

The first samples were from the Geokinetics In Situ Oil Shale Project, located in the Uinta Basin, Utah. This project was a cooperative venture between Geokinetics Inc. and the U.S. Department of Energy. Operated during the late 1970's and early 1980's, the Geokinetics project utilized a horizontal modified in situ (HMIS) system, whereby near surface oil shale was fractured and ignited. Driven by forced air induction, a burn front was forced horizontally through the in situ retort (Lekas, 1979). Samples were collected from core holes drilled in 1980 from Geokinetics retort 16.

The second set of samples were from the Rio Blanco Oil Shale Company's retort 1 located in the Piceance Creek Basin, Rio Blanco County, Colorado on the Federal Prototype Oil Tract C-a. The Rio Blanco Oil Shale Company's retort 1 was of a Vertical Modified In Situ (VMIS) retort type. In a VMIS retort, a retort is constructed by mining and blasting to create a chimney of oil shale approximately 60 feet square and 400 feet high. The oil shale is then ignited, with the burn front proceeding vertically through the retort. A more complete discussion of the Rio Blanco Oil Shale Company's process and retort 1 can be found in Mason and Trudell (1989).

The third set of samples was from the U.S. Department of Energy's reference shale program. Green River Formation oil shale was obtained from the Exxon Colony Oil Shale Mine near Parachute, Colorado and retorted utilizing the Paraho Inclined Fluidized Bed Process by the Western Research Institute in Laramie, Wyoming. The Paraho Inclined Fluidized Bed Process was operated in direct and indirect heating modes and combusted in an inclined fluidized bed. Essington et al. presented a detailed description of the operating conditions under which the oil shale materials were processed (Essington et al., 1987). For detailed information pertaining to sample location as well as chemical and physical characteristics of the DOE Reference Shale materials, see Miknis and Robertson (1987). Location of sample sources are shown on Figure 1.

Mineral identification was completed by: optical microscopy using a polarizing, transmitted light, petrographic microscope with standard 30μ (thickness) thin sections and by X-ray Diffraction (XRD) using an automated powder diffractometer using nickel-filtered copper Kα radiation.

Mineralogy

Unprocessed Oil Shale

Mineralogy of the Green River Formation has been a topic of study for many years with more than 80 minerals identified in its various surface and subsurface localities in Colorado, Utah, and Wyoming (Milton, 1977). Stratigraphic mineralogical variations within the Green River Formation have been well documented. For this study, two groups of minerals were considered rele-
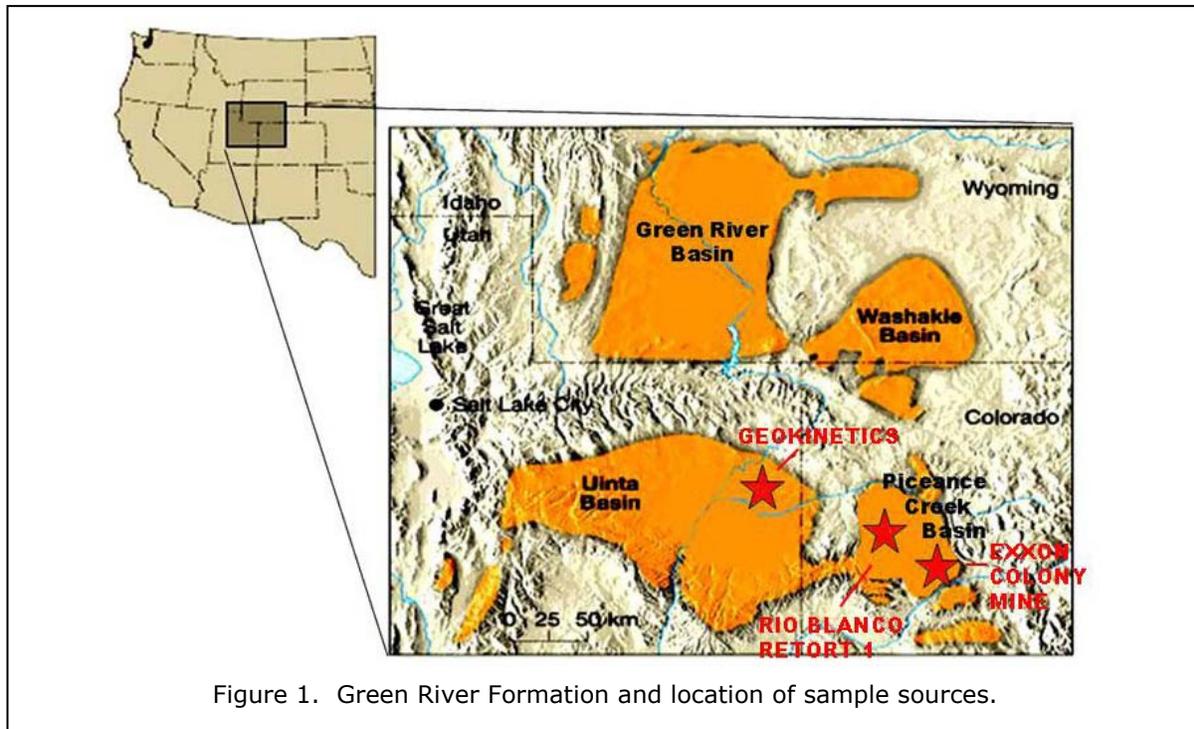
Figure 1. Green River Formation and location of sample sources.

vant, silicates (quartz, feldspars, analcime, and clay minerals) and nonsilicates (minerals of the calcite and dolomite groups). Although the formation contains numerous other minerals and locally these can constitute a large percentage of the formation, in the oil shale zones that were sampled, minerals other than the silicates and carbonates did not appear to affect the resultant mineral products. The generalized minerals of the Green River Formation are shown in Table 1.

Processed Oil Shale

Mineralogy of Green River Formation is radically changed when the raw oil shale is subjected to the extreme temperatures of processing. Smith et al. (1978) concluded that temperatures of up to 1200° C are achieved during in situ retorting. Maximum temperatures reported for the Paraho process were slightly lower, achieving nearly 1150° C (Essington et al., 1987).

Mineral reactions from high temperature oil shale retorting can be summarized by two general steps, (1) decomposition of raw minerals and (2) crystallization from the melt. Park et al. (1979) summarized car-

bonate mineral decomposition during oil shale processing. Complete decomposition of carbonate minerals and silicate minerals form a pyrometamorphic melt containing the principle ions: Ca^{2+}, Na^{+}, Mg^{2+}, Fe^{2+}, Fe^{3+}, K^{+}, Si^{4+}, Al^{3+}, O^{2+}, and CO_3^{2-}. Trace elements are abundant in the Green River Formation and are undoubtedly present in the melt, but low abundances make their contribution to the crystallization of new minerals negligible. The generalized minerals identified in processed Green River Formation oil shale are shown in Table 2.

Silicate mineral products of high temperature oil shale processing fall into several general types; olivine group, melilite group, ortho- and clinopyroxenes, amphibole, feldspar group, quartz, and clay minerals. Amorphous silica (glass) is also common product in oil shale that has been processed at high temperatures then cooled rapidly. Although variation within the mineral groups can be in part due to minor differences in the composition of the raw oil shale, the final mineral suite appears to vary very little when examining material from different processes and localities.

3

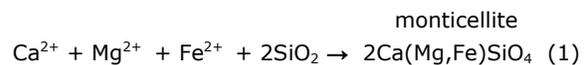**Table 1. Minerals identified in Green River Formation oil shale.**

MINERAL	CHEMICAL FORMULA	ABUNDANCE (%)
Dolomite Group	$X(CO_3)_2$	10 - 60
Calcite Group	XCO_3	5 - 40
Quartz	SiO_2	10 - 30
Feldspars	$YA1SiO_3$	10 - 30
Clay Minerals: chlorite, illite, smectite, MLC	X-Y-Al-Si-O-H	1 - 30
Rare Carbonates: dawsonite, nahcolite, trona, shortite	$NaAl(OH)_2CO_3$, $NaHCO_3$, $Na_3(CO_3)HCO_3.2H_2O$, $Na_2CO_3 \cdot 2CaCO_3$	<1 - 15
Analcime	$NaA1Si_2O_6 \cdot H_2O$	<1 - 5
Misc. Minerals: pyrite, apatite, halite, biotite, aragonite, etc.	FeS_2, $Ca_{10}F(PO_4)_6$, $NaCl$, $K(Mg,Fe)_3(A1Si_3O_{10})(OH)_2$, $CaCO_3$	<1 - 5

Where: X = Ca,Mg,Fe; Y = Na,Ca,K,NH$_4$

Equations summarizing the formation of silicate minerals identified in processed oil shale can be generalized by an equation representative of each mineral group. Calculation of Gibbs free energy values used referenced ΔG_f° data (Woods and Garrels, 1987). Equation (1) illustrates the crystallization of the Ca-olivine, monticellite from a melt.

Figure 2 is a photomicrograph of monticellite (or merwinite?) identified by thin section in combusted Green River Formation Oil shale Equation (2) illustrates the formation of the pyroxene augite from monticellite.   The slightly positive value (+2.80 kcal) would seem to favor the augite, although very slightly.

$$\text{monticellite}$$
$$Ca^{2+} + Mg^{2+} + Fe^{2+} + 2SiO_2 \rightarrow 2Ca(Mg,Fe)SiO_4 \quad (1)$$

where:

Table 2.   Silicate minerals identified in combusted Green River Formation oil shale.

MINERAL	SILICATE TYPE	CHEMICAL FORMULA
Olivine Group: Monticellite-Merwinite Forsterite-Fayalite	Neso	$CaMgSiO_4$-$Ca_3(MgSiO_4)_2$ Mg_2SiO_4 - Fe_2SiO_4
Melilite Group: Akermanite-Gehlenite	Soro	$Ca_2Al_2Si_2O_7$-$Ca_2MgSi_2O_7$
Augite-Diopside	Ino (single)	$XY(Z_2O_6)$-$CaMgSi_2O_6$
Actinolite-Tremolite	Ino (double)	$Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$ - $Ca_2Mg_5Si_8O_{22}(OH)_2$
Clintonite	Phyllo	$Ca_2(Mg,Fe)_4Si_2Al_6O_{20}(OH)_4$
Feldspar Group: Plagioclase, K-feldspar	Tecto	$NaAlSi_3O_8$ - $CaAlSi_3O_8$ $KAlSi_3O_8$
Quartz	Tecto	SiO_2
Glass	Amorphous	SiO_2

Where: X = Ca,Na; Y = Mg,Fe,Al

$\Delta G_R = \dfrac{[-512.12]}{[-132.2][-108.8][-22.0][-204.7]^2} = -160.28$ kcal

Figure 3 is a photomicrograph of augite surrounded by melilite identified by thin section in processed oil shale. Figure 4 is a SEM photograph illustrating the typical mineral composition of a disequilibrium mixture of augite, amphibole (actinolite), and melilite.

monticellite   augite

$Ca(Mg,Fe)SiO_4 + SiO_2 \rightarrow (Ca,Mg,Fe)(SiO_3)_2$ (2)
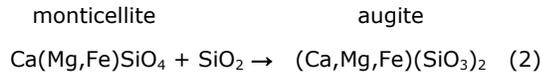
where:

$\Delta G_R^\circ = \dfrac{[-724.6]}{[-517.1][-204.7]} = +2.80$ kcal

The formation of the amphibole actinolite from augite + periclase + water is shown in equation (3). The very positive value (+1519.864 kcal) would therefore, not kinetically favor the formation of actinolite. Actinolite is rare in processed oil shale; however, actinolite fills a niche in the reaction scheme and has been identified in reacted oil shale (Mason and Trudell, 1989). Gibbs Free Energy calculations for actinolite clearly indicate that actinolite is not kinetically favored, therefore it would be expected to be a rare product.

Figure 5 is a photomicrograph of an amphibole identified in thin section in processed oil shale.

augite

$4(Ca,Mg,Fe)(SiO_3)_2 + 3(Mg,Fe)O + H_2O \rightarrow$
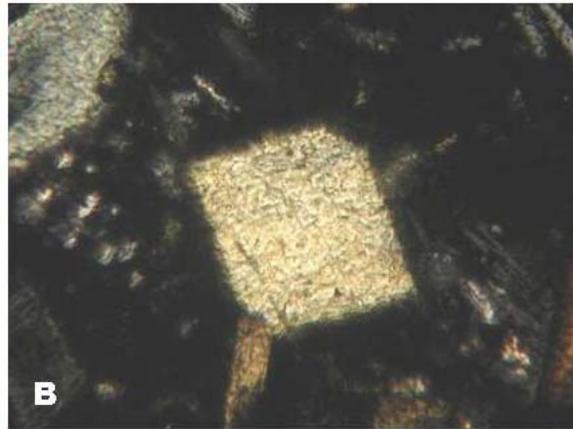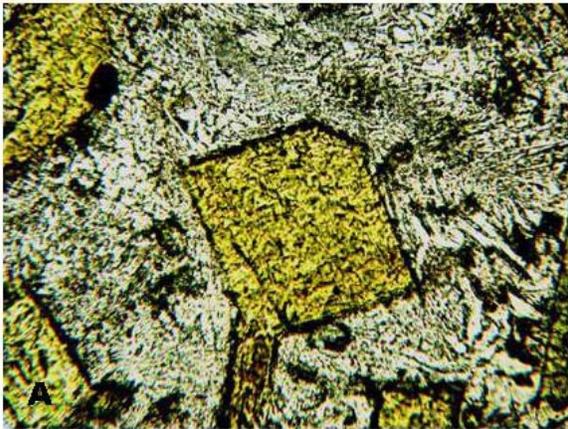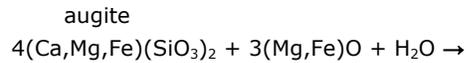

Figure 2. Monticellite in plane-polarized light (A) and with crossed polars (B) (x 400). Sample from Geokinetics, retort 16-11 , 45.0 feet.
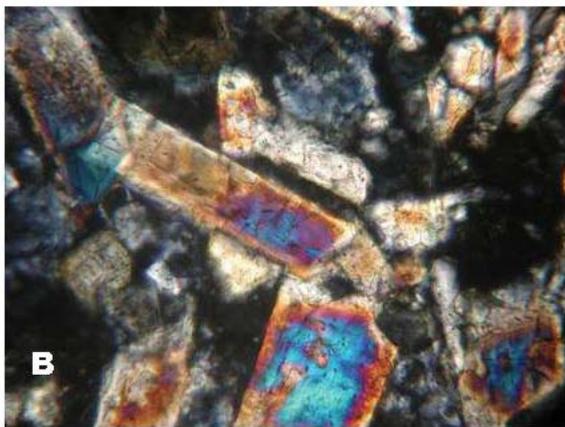

Figure 3. Augite surrounded by melilite, in plane-polarized light (A), with crossed polars (B) (x 400). Sample from Rio Blanco, PBC-II, 554.1 feet.
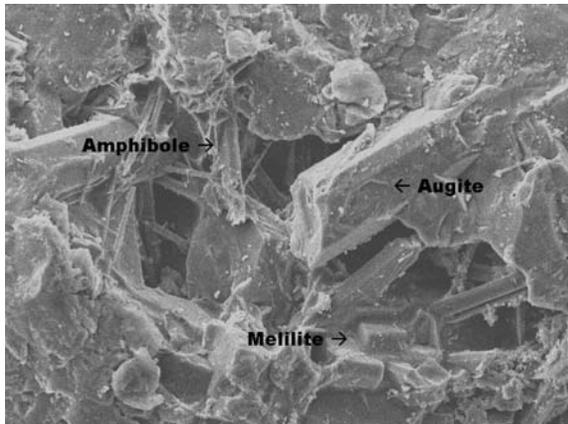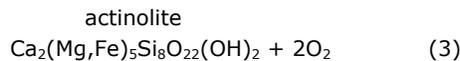
Figure 4. SEM photograph of a disequilibrium crystal mixture of amphibole, augite and melilite from processed oil shale, magnification 1000X. Sample from Geokinetics retort 16, depth 45.0 feet.
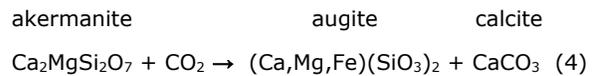
actinolite
$$Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2 + 2O_2 \qquad (3)$$

where:

$$\Delta G_R^\circ = \frac{[-2625.5][O]^2}{[-724.6][-108.8]^3[-54.636]} = +1519.864 \text{ kcal}$$

Melilite, a solid solution of akermanite-gehlenite, is a comparatively rare mineral in nature; however, it is found in abundance in processed oil shale. Because of the incorporation of Al^{3+} into the structure of gehlenite, two possible reactions for the formation of melilite are shown. The formation of akermanite is illustrated in equation (4) The formation of gehlenite is illustrated in equation (5). Both equations for the formation of the end members of the melilite group illustrate that augite would be the slightly kinetically favored product. However, the abundance of the melilite identified in processed oil shale and th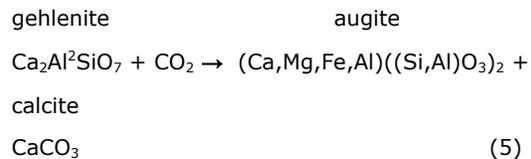e degree of mineral adsorption that can be observed between these two minerals, clearly indicate that the kinetic boundary between the two is a very tenuous one.

Figure 6 is a photomicrograph of melilite identified by thin section in processed oil shale. Figure 7 is a Scanning Electron Microscope (SEM) photograph of melilite illustrating tetragonal mineral habit.

akermanite   augite   calcite

$$Ca_2MgSi_2O_7 + CO_2 \rightarrow (Ca,Mg,Fe)(SiO_3)_2 + CaCO_3 \quad (4)$$

where:

$$\Delta G_R^\circ = \frac{[-724.6][-269.9]}{[-879.1][-94.254]} = +21.146 \text{ kcal}$$

gehlenite   augite

$$Ca_2Al^2SiO_7 + CO_2 \rightarrow (Ca,Mg,Fe,Al)((Si,Al)O_3)_2 +$$

calcite

$$CaCO_3 \qquad\qquad\qquad\qquad (5)$$

where:

$$\Delta G_R^\circ = \frac{[-724.6][-269.9]}{[-906.1][-94.254]} = +5.854 \text{ kcal}$$

Mason and Trudell (1989) reported clay minerals in retorted oil shale that was believed to be heat-altered incompletely decomposed oil shale that had fallen into the retort cavity. They identified a clay mineral which they believed to be a heat-altered smectite mineral that would not accept ethylene glycol into its structure. From additional study, it is now believed that unidentified mineral to be a Ca-analog to the micas called clintonite. The formation of clintonite from actinolite is illustrated in equation (6). The very positive value of this reaction would seem to indicate that a Ca-
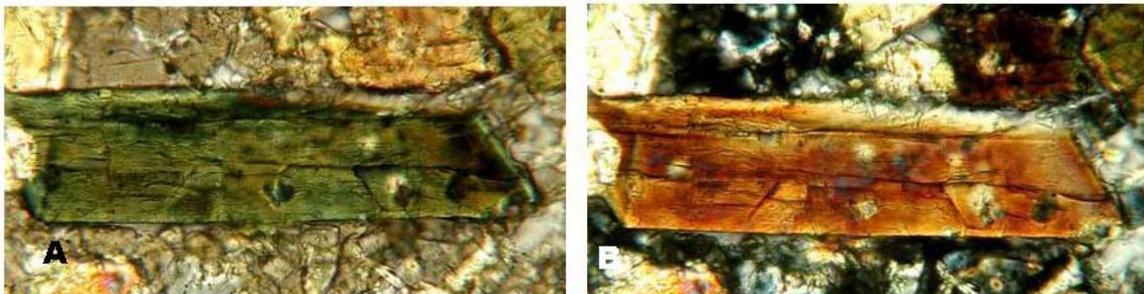

Figure 5. Amphibole in plane-polarized light (A) and with crossed polars (B) (x 100). Sample from Geokinetics, retort 16-11, 45.0 feet.

6

Figure 6. Melilite (akermanite) in plane-polarized light (A) and with crossed polars (B) (x 400). Sample from Geokinetics retort 16-11, 46.3 feet.

Figure 7. SEM photograph of a crystal of melilite illustrating tetragonal crystal habit from processed oil shale, magnification 1000X. Sample from Geokinetics retort 16, depth 45.0 feet.

analog mica would be a kinetically favored product from the processing of oil shale.

Figure 8 is a photomicrograph of the Ca-mica clintonite identified by thin section in processed oil shale. Figure 9 is an SEM photograph of clintonite in processed oil shale.

clintonite
$$Ca_2(Mg,Fe)_{4.6}Al_{1.4}(Si_{2.5}Al_{5.5}O_{20})(OH)_4 + (Mg,Fe)O + 10SiO_2 \rightarrow$$

actinolite   sillimanite
$$Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2 + 4Al_2SiO_5 + H_2O \quad (6)$$

Where:

$$\Delta G_R^o = \frac{[-582.9^*]^4[-54.636]}{[-1410.0][-136.1][-204.7]^{10}} = +1207.764 \text{ kcal}$$

* estimated value using phlogopite

Feldspar of unknown composition was reported by Smith et al. (1978) in processed oil shale. Mason and Trudell (1989) reported altered feldspar that appeared to be of intermediate composition between plagioclase and orthoclase. Seck (1971) reported that a field of two feldspars can exist

Figure 8. Clintonite in plane-polarized light (A) and with crossed polars (B) (x 100). Sample from Rio Blanco, PBC-1, 518.3 feet.
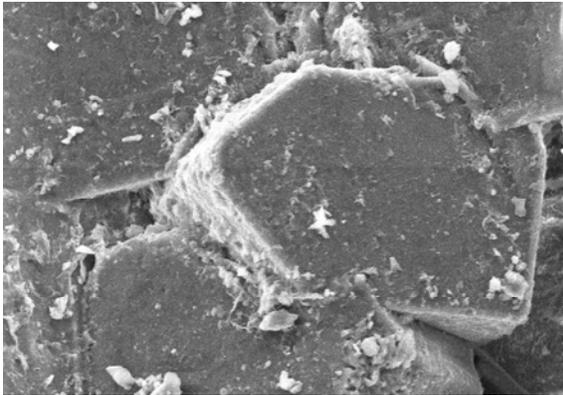
Figure 9. SEM photograph of clintonite from processed oil shale, magnification 1000X. Sample from Geokinetics retort 16, depth 45.0 feet.

at temperatures of greater than 650°C (P_{H20} = 1kbar) and become an indistinguishable mixture above 900°C (P_{H20} = 1kbar)[20]. It does not seem improbable that an intermediate phase having the complex structural arrangement of the feldspar family, yet sharing Ca, Na, and K in some type of cation substitution could be formed as a result of oil shale processing. Equation (7) illustrates a possible formation of the intermediate feldspar reported in processed oil shale. No thermodynamic data for K-anorthoclase could be found in the literature. To facilitate calculations, a value of -890.0 kcal was assumed. This value was selected as being in the same range as all documented feldspar values. Regardless of the value selected, the Gibbs free energy calculations indicated that the resultant value for the equations would only have either a very slight positive or negative value. Therefore, it can be concluded that the feldspar reaction would not favor, to any substantial degree, any of the feldspar products over one another during the processing of oil shale but would probably be controlled by the elemental composition of the reactants.

plagioclase   orthoclase   K-anorthoclase

$$(Na,Ca)AlSi_3O_8 + KAlSi_3O_8 \rightarrow 2(Na,Ca,K)AlSi_3O_8 \quad (7)$$
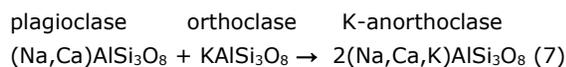
where:

$$\Delta G_R^\circ = \frac{[-890^*]^2}{[-884.8][-893.6]} = +1.6 \text{ kcal}$$

* estimated value

Discussion

In Bowen's reaction series, temperatures decrease from top to bottom. Minerals in the series that crystallized at higher temperatures react with the remaining magma as it cools resulting in the formation of minerals lower in the series. One side of the series illustrates how this process results in formation of solid solution in the plagioclase feldspars, with Ca-feldspar at the high temperature end and Na-feldspar at the low temperature end. This branch is called a Continuous reaction series because as the magma cools, sodium and silicon progressively substitute for calcium and aluminum within the plagioclase crystal structure. Decreasing temperatures causes the crystal structure to shrink slightly, thus favoring sodium over calcium because of its smaller atomic radii. Additionally, this substitution results in a steady increase in the ratio of silicon to oxygen.

The other branch of the reaction series, called a Discontinuous reaction series, has iron- and magnesium-rich minerals all with different crystal structures. A given mineral must therefore be completely melted before it can be reconstructed as the next lower mineral in the series. The minerals high on the branch are relatively unpolymerized, whereas those low on the branch are more polymerized. This, too, results in an increase of silicon:oxygen ratios as more oxygens are shared. Aluminum, for minerals on the discontinuous branch of the reaction series, was probably derived from the feldspar minerals on the continuous branch of the reaction series, which were in turn left slightly aluminum poor to form the altered feldspar phase (K-anorthoclase) reported.

The mineral structures represented in Bowen's reaction series can be interpreted as having a temperature - structure relationship. The hottest temperatures are represented by the simplest silicate structures, nesosilicates ($(SiO_4)^{4-}$) which consist of independent silica tetrahedra and are represented by olivine and olivine-type minerals. Increasing complexity of structures repre-

sents lower temperatures and/or longer cooling times. The reaction series progresses from nesosilicates to single chain inosilicates $((SiO_3)_2^{4-})$ represented by clino- and orthopyroxenes, which is then followed by double chain silicates $((Si_4O_{11})^{6-})$ represented by the amphiboles. Inosilicates are followed the phyllosilicates $((Si_2O_5)^{2-})$ which are sheet silicates represented by the micas. Ultimately, the Discontinuous reaction series branch will produce tectosilicates $((SiO_2)^0)$ which are complex 3-dimensional frameworks represented by K-feldspar and quartz. The different silicate structures in the Discontinuous reaction series portion of Bowen's Reaction series represent increased silica polymerization with as a direct consequence of temperature and (cooling) time. Although a significant degree of overlapping of the different silicate forms exists, a temperature - structure relationship can be recognized.

Oil shale processing produces temperatures on par with naturally occurring magma 1200°C and 1150°C respectively (Park et al., 1979). Therefore, given an adequate supply of silica and cations, a fractional crystallization scheme will develop when the molten material cools. Identification of minerals that have similar silicate structures to naturally occurring reaction series can be recognized in processed oil shale. As in natural magmas, when the shared arrangement of silica and oxygen become more complex, i.e. increased polymerization, an overall decrease in the silica:oxygen ratio is achieved.

During the cooling of most natural magmas, adequate time allows the establishment of chemical equilibrium in the system. At the end of the cooling phase, any unused silica will remain as quartz. The cooling of oil shale molten material, on the other hand, displays a very different scenario. Rapid cooling and irregular heat dispersal within the retort contributes to disequilibrium. The identification of minerals similar in silica structure to the minerals of Bowen's reaction series leads to the conclusion that the silicate minerals that formed during the cooling of molten oil shale probably underwent a similar fractional crystallization

process. The primary difference lies in the basic chemical difference that molten oil shale is strongly biased toward Ca-analogs because of the composition of the original raw Green River Formation oil shale. However, the presence of H_2O and organic carbon must certainly play a significant role in the establishment of thermodynamic equilibria and redox interactions between organics, H_2O, and the minerals. The significance of all these factors are yet to be studied.

The most notable deviation from the minerals and silicate structures identified in processed oil shale versus a naturally occurring magma is the identification of a group silicate or sorosilicate. Sorosilicates $((Si_2O_7)^{6-})$ have two silicon atoms, each with three oxygen atoms bonded to them while sharing a seventh oxygen atom. Sorosilicates are the first structure in the reaction series displaying polymerization of silica. Sorosilicates are abundantly represented in processed oil shale by a solid solution of the minerals akermanite-gehlenite $(Ca_2Al_2SiO_7-Ca_2MgSi_2O_7)$ often referred to as melilite. The mineral group was placed second in the reaction series directly after the nesosilicate minerals. As a consequence of disequilibrium, often several different mineral phases are found within proximity to one another. Although the kinetics of the mineral reactions are attempting to dictate increasing silica polymerization, this orderly fractional crystallization scheme is probably rarely, if ever achieved. Instead, the minerals identified in processed oil shale appear to be a crystalline hodgepodge, having all the elements of fractional crystallization, but jumbled by disequilibrium; a probable consequence of quenching.

Although not positively identified in processed oil shale samples obtained for this study, a Ca-analog to the micas can be speculated to be present, especially in the more thermally insulated or deeper portions of an in situ retort. Clintonite, $Ca_2(Mg,Fe)_{4.6}Al_{1.4}(Si_{2.5}Al_{5.5}O_{20})(OH)_4$ is commonly encountered in zones of metamorphosed impure limestone and dolostone, especially skarn deposits. Mason and Trudell[6] reported actinolite and mullite in
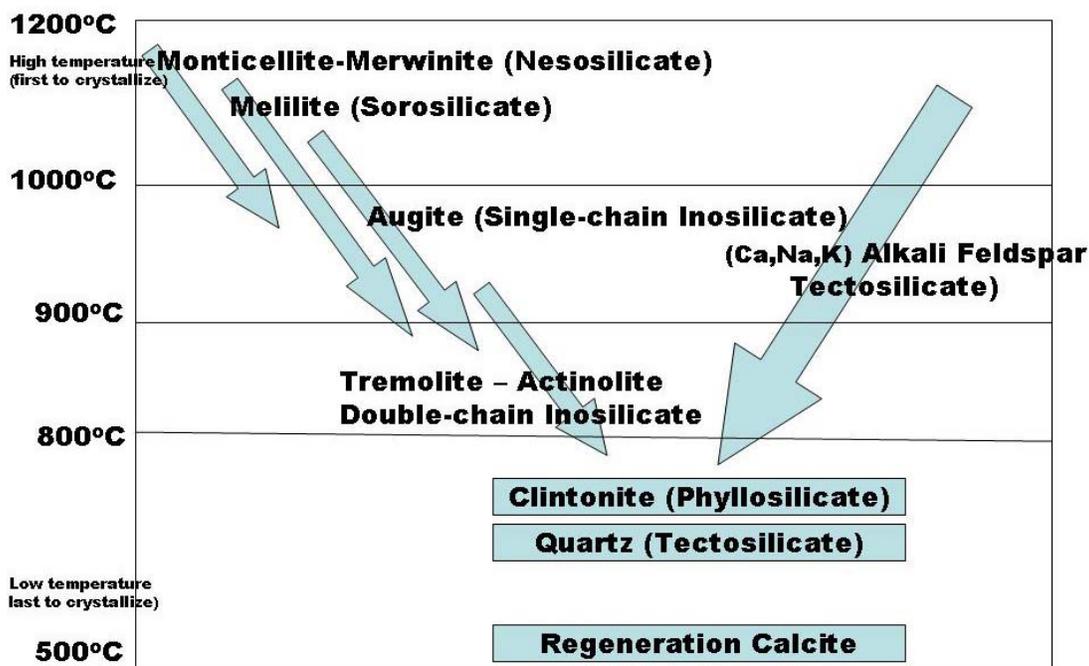
Figure 10. Oil shale reaction series based upon silicate fractional differentiation.

samples studied from the Rio Blanco Oil Shale Company Vertical Modified In Situ retort. Sillimanite Al_2SiO_5 has a very similar chemistry and morphology to mullite. Clintonite + periclase + SiO_2 will form actinolite and sillimanite. It therefore seems possible that clintonite, actinolite, and sillimanite are all possible products of oil shale processing, but due rapid cooling and channeling of the burns within the retort, silica deficiency in the molten material perhaps due to unmelted silica-rich material makes these minerals very rare. The consumption of all available silica would contribute also to the quenching of the oil shale reactions before the last silicate mineral in the sequence could form. Figure 10 illustrates the minerals of the oil shale reaction series, arranged with respect to fractional differentiation of the silicate structure (i.e. with respect to silicate polymerization) as Bowen's reaction series.

Conclusions

Similarities were observed between Bowen's reaction series and minerals gener-

ated by the high temperature processing of Green River Formation oil shale. The crystallization sequence for molten oil shale resembles an alkaline Ca-rich magma; however, thermodynamic and kinetic disequilibrium is the rule rather than the exception. Because of disequilibrium in the system, more than one crystalline phase may exist in proximity to other phases.

In the crystallization sequence, the hottest temperatures and associated cooling result in increased polymerization of silica. Starting with a silica:oxygen ration of 1:4 and ending with a silica:oxygen ration of 1:2. This sequence, in terms of silicate structure is: nesosilicate → sorosilicate → single chain inosilicates → double-chain inosilicates → phyllosilicate → tectosilicate.

An oil shale reaction series, paralleling Bowen's Reaction Series, consisting of silicate minerals biased toward calcium analogs expresses the products generated from oil shale processing. This reaction series can be expressed as monticellite → akermanite-gehlenite → augite-diopside → actinolite-

tremolite → clintonite, the Ca-analog to mica forming the lowest member of the processed oil shale mineral suite.

References

Bowen, N.L., *The Evolution of the Igneous Rocks*, Princeton University Press, Princeton NJ, 332 p. 1928.

Essington, M.E., L. K. Spackman, J. D. Harbour, and K. D. Hartman, "Physical and Chemical Characteristics of Retorted and Combusted Western Reference Oil Shale," U.S. DOE Report DOE/MC/11076-2453, Laramie, Wyoming, 156 p., 1987.

Lekas, M.A., "The Geokinetics In Situ Oil Shale Recovery Project, Second Annual Report," U.S. DOE Report LETC/10787-25, Laramie, Wyoming, 1979.

Mason, G.M. and L. G. Trudell, "Postburn Characterization of a Modified In Situ Oil Shale Retort, Piceance, Creek Basin, Colorado," In Situ, v. 13, (1&2), pp. 79-99, 1989.

Miknis F.P. and R. E. Robertson, "Characterization of DOE Reference Oil Shales: Mahogany Zone, Parachute Creek Member, Green River Formation and Clegg Member, New Albany Shale," U.S. DOE Report DOE/FE/1107-2526, Laramie, Wyoming, 48 p., 1987.

Milton, C., "Green River Mineralogy," Mineralogical Record, v.8, pp. 368-379, 1977.

Park, W.C., A. E. Linderamanis, and G. A. Robb, "Mineral Changes During Oil Shale Retorting," In Situ, v. 3(4), pp. 353-381, 1979.

Seck, H.A., "Koexistierend Alkali-feldspate und Plagioklase im System $NaAlSi_3O_8$-$KAlSi_3O_8$-$CaAlSi_3O_8$-H_2O bei temperaturen von 650℃ bis 950℃. N. Jahrb. Minerl. Abh. 115, 315, 395, 1971.

Smith, J.W. and W. A. Robb, "Ankerite in Green River Formation's Mahogany zone," Journal of Sedimentary Petrology, v.36, pp. 486-490, 1966.

Smith, J.W., W. A. Robb, and N. B. Young, "High Temperature Mineral Reactions of Oil Shale Minerals and their Benefit to Oil Shale Processing in Place," Proceedings of the 11th Oil Shale Symposium, J. H. Gary, editor, Colorado School of Mines, Golden, Colorado, pp. 100-112, 1978

Trudell, L.G., T. N. Beard, and J. W. Smith, "Green River Formation Lithology and Oil Shale Correlations in the Piceance Creek Basin, Colorado," U.S. Bureau of Mines Report of Investigations 7357, 1970.

Woods, T.L. and R.M. Garrels, *Thermodynamic Values at Low Temperature for Natural Inorganic Materials: An Uncritical Summary*, Oxford Univer. Press, 242p., 1987.