GLY 4200C LAB EXERCISE 7

## HALIDES, SULFATES, AND BORATES

Halides

Halide minerals contain the anions  $F^-$ ,  $CI^-$ ,  $Br^-$ , or  $I^-$ . There are more than one hundred forty known halides but only a few are important. Because most of the halide ions are spherical in crystalline materials, the packing is of a highly symmetric nature. The bonding is almost purely ionic. If the cation is small and strongly polarizing the symmetry will be reduced. (Example: Cryolite Na<sub>3</sub>AlF<sub>6</sub> is monoclinic).

The halides are of low to moderate hardness. They occur as XZ or  $XZ_2$  structures in many cases, although other formulas are possible (X = metal cations, Z = halide anion). The halide minerals are often found in evaporite deposits.

	XZ		Other forms
HALITE NaCl Cryolite Na <sub>3</sub> A	HALITE	NaCl	Cryolite Na <sub>3</sub> AlF <sub>6</sub>
SYLVITE KCl	SYLVITE	KCl	

 $XZ_2$ 

FLUORITE CaF<sub>2</sub>

## **Sulfates**

The SO<sub>4</sub><sup>2-</sup> group characterizes the sulfates. In the sulfur group sulfur is 6+, a small (0.03 nm) highly polarizing cation. The radius ratio with oxygen is 0.214, within the range for tetrahedral coordination. These groups are very strongly bonded and do not break up during most <u>chemical</u> reactions. Anaerobic bacteria can break the sulfur to oxygen bond, however.

The most important anhydrous sulfate group is the barite group. This group has large divalent cations in XII coordination to oxygen. Similar structures are found in manganates,  $MnO_4^{2-}$  and chromates,  $CrO_4^{2-}$ . In the anhydrite structure calcium ions are in eight coordination to oxygen.

The most important hydrous sulfate is gypsum. The structure consists of calcium ions strongly bonded to sulfate groups parallel to  $\{010\}$ . These layers are separated by sheets of water molecules. Bonds to the water molecules are weak, which explains the perfect cleavage along  $\{010\}$  in gypsum. Gypsum has secondary cleavage along  $\{100\}$ , and along  $\{011\}$ . These lead to a number of varieties.

Examine the following specimens:

Barite Group		Hydrous Sulfates		
BARITE	$BaSO_4$	GYPSUM	$CaSO_4 \cdot 2 H_2O$	
CELESTITE	$SrSO_4$	varieties Satin spar, alabaster,		
	selenite, massive			
Anhydrite Group		Alunite	$KAl_3(SO_4)_2(OH)_6$	
		Polyhalite	$K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$	
ANHYDRITE	$CaSO_4$			

## **Borates**

The basic borate group is  $BO_3^{3-}$ , which is a trigonal planar group. The oxygens can be shared. In fact the borates are usually polymers, or extended structures with many  $BO_3^{3-}$  groups linked together. Boron also forms  $BO_4^{5-}$  groups which are tetrahedral.

Examine the following specimens:

KERNITE	$Na_2B_4O_6(OH)_2$ · $3H_2O$
BORAX	$Na_2B_4O_5(OH)_4$ · $8H_2O$ Note: Borax readily alters to tincalconite,
	$Na_2B_4O_5(OH)_4$ · $3H_2O$
Ulexite	$NaCaB_5O_6(OH) \cdot 5H_2O$
Colemanite	$CaB_3O_4(OH)_3 \cdot H_2O$

## **Reference material in text**

Klein and Dutrow, Chapter 16, pp. 374-375 and 393-398 has information concerning halide minerals. Chapter 17, pp. 403-405 and 420-425 has information about sulfate minerals. Chapter 17, p. 403-405 and pp. 416 - 420 has information about borate minerals. These pages should be consulted while doing this laboratory exercise.

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