

Chemical Composition, Polymorphism, Atomic Substitution, Isomorphism and Solid Solution

The composition of minerals was originally determined by various wet chemical analysis techniques. These days analysis is done mainly by beam analytical instruments: electron microprobes and energy dispersive x-ray analyzers.

These instruments work by using an energy beam (high energy electrons) fired at a mineral grain. The mineral emits lots of things when struck by this beam including low energy x-rays. By measuring the energy levels or the wave length of the emitted x-rays one can determine what kind of elemental components (qualitative analysis) and how much of each component (quantitative analysis) is present. We may be able to use this instrumentation later in the semester.

The chemical analysis of a mineral shows the elements that are present, and how much of each, but not how they are combined in the structure of the mineral. The results of chemical analyses are presented in ***weight percent (wt %)***. In order to determine the formula for the mineral, wt % must be converted to ***atomic proportions***. Dividing the wt % of each element by the atomic weight of that element and then determining the relative proportions do this. See the procedure for a specimen of ***marcasite***

<u>Element</u>	<u>Wt %</u>	<u>Atomic Weight</u>	<u>Atomic Proportions</u>
Fe	46.55	55.85	0.834
S	53.05	32.07	1.655
Total	99.6		

If we multiply each of the atomic proportions by 1/0.834 then the relative proportions are more obvious

$$0.834 \times (1/0.834) = 1;$$

$$1.655 \times (1/0.834) = 1.988$$

The formula for marcasite is FeS₂. Note that some analytical error can be expected and that an analysis between 99.5 and 100.5 (total wt %) is probably just that, analytical error.

We can also calculate the expected percent composition by the reverse procedure. Since the atomic weight of Fe is 55.85 and Sulfur is 32.07 then the formula weight of FeS₂ is: 55.85 + 2(32.07) = 119.99.

$$\%Fe = 55.85/119.99 \times 100 = 46.54$$

$$\%S = 64.14/119.99 \times 100 = 53.46$$

Polymorphism (See S&S Field Guide, pp 27-31)

1. The analyses for several other samples of marcasite (in wt %) are presented below.

	1	2	3	4	5
Fe	46.54	46.55	46.53	47.22	46.56
S	53.46	53.05	53.30	52.61	53.40
	100.00	99.60	99.83	99.83	99.96

a. What are the atomic and relative proportions (A-P/R-P) of Fe and S in each sample and what is the chemical formula for each sample of marcasite?

	A-P/R-P 1	A-P/R-P 2	A-P/R-P 3	A-P/R-P- 4	A-P- 5/RP- 5
Fe					
S					
Chemical Form					

b. What do you think is the reason for variation in analyses? Do you think there is any atomic substitution or is the composition of marcasite fixed?

c. Iron always occurs as either the ferrous, Fe^{+2} or ferric, Fe^{+3} ion in nature. Is marcasite a simple ionically bonded mineral phase? What type of bonding do you think occurs in this sulphide mineral? Hint: what is marcasite's luster?

d. Is there another common sulphide mineral closely related (in chemical composition) to marcasite? What is it? What is that relationship called?

Atomic substitution and Solid Solution

2. Let's take a look at chemical composition in a more complicated material system, the zinc sulphide mineral, Sphalerite.

	1	2	3	4
Fe	.015	7.99	11.05	18.25
Mn	-	-	-	2.66
Cd	-	1.23	0.3	0.28
Zn	66.98	57.38	55.89	44.67
S	32.78	32.99	32.63	33.57
	99.91	99.59	99.87	99.43

As the analyses indicate Sphalerite may be almost pure zinc sulphide or may contain a lot of iron and small amounts of other transition metals.

- a. What is the chemical formula shown for Sphalerite in your R&M guide? What type of bonding do you think exists in Sphalerite?

- b. Calculate the atomic proportions (round off to the 0.001 place) for each element in each analysis and enter it in the table below

	1	2	3	4
Fe				
Mn				
Cd				
Zn				
Total metals (add above columns)				
S				

- c. What are the relative proportions of total metals to sulfur for each sample?

- d. What are the (most probable) valences of each element?

- e. For analysis #4 calculate the decimal fraction of each metal (omit Cd) relative to total metals (divide each atomic proportion by total metals atomic proportion).
- f. How might you write the chemical formula for this sample of Sphalerite to show actual metals composition?
- g. Do ZnS and FeS (typically written Fe_{1-x}S , what is this mineral?) share the same crystal structure? What is this chemical relationship called?