MINERAL OXIDATION

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Abstract

Mineral oxidation is of two radically different kinds; one is the well known oxidation during weathering which involves addition of oxygen and the other is the little known oxidation during anamorphism which involves elimination of hydrogen (but no addition of oxygen). The first destroys the primary mineral and forms new ones; the second merely modifies the primary mineral but does not destroy it. Examples of the second process are described and illustrated by diagrams.

It is very well known that oxidation is one of the important chemical processes of katamorphism, especially of weathering, but it is not as well known that the same chemical process may result from anamorphism, if conditions are favorable. However, oxidation during weathering destroys the old compounds and produces new ones, while oxidation during anamorphism may leave the old compounds intact with their characteristic crystal structures (almost) unmodified and their properties modified in no very radical way. It is possible to distinguish between these two cases by noting that oxidation during weathering is an oxidation *of* (one or more) minerals, while oxidation during anamorphism is an oxidation *in* (one or more) minerals. This difference will be more easily understood by describing a few illustrations.

Oxidation During Weathering

Weathering destroys siderite ($FeCO_3$) producing CO_2 and hematite (Fe_2O_3) or limonite ($2Fe_2O_3 \cdot 3H_2O$?) by oxidation (and hydration) of the iron. In a similar way it destroys pyrite, or marcasite (FeS_2), producing sulfuric acid and hematite or limonite by oxidation (and hydration). Or, again, it destroys olivine, producing serpentine and limonite by oxidation (and hydration).

Mason[1] has shown that minerals containing both iron and manganese are oxidized in two stages, all the iron being oxidized before oxidation of the manganese begins.

In all of these cases (and many more) the original mineral is destroyed and one or more new minerals are formed by oxidation, and in all these

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[1] Mason, F., *Geol. För. Förh. Stockholm*, **63,** 117 (1941).

cases oxygen is added to the original mineral. The processes are so well known that further description is needless.

Oxidation During Anamorphism

When a mineral which contains ferrous iron and also hydroxyl (or, perhaps, in some cases, H_2O) is heated artificially or in nature under conditions which permit hydrogen to escape, the hydroxyl radical may lose hydrogen and become an atom (or ion) of oxygen, the valence bond previously satisfied by hydrogen now serving to convert an adjoining atom (or ion) of iron from the ferrous to the ferric state. The change from the hydroxyl radical to the oxygen atom is accomplished with only a little change of size and little, if any, change of shape, or position, in the crystal lattice; likewise, the change from a ferrous to a ferric atom is accomplished with only a little change of size and little, if any, change of shape or position of the iron atom in the crystal lattice. Accordingly, the oxidation of the iron occurs *inside* the mineral, with little, if any, change in its crystal structure—that is, the mineral is not destroyed, nor even changed, in any fundamental sense. Moreover, the oxidation of the iron can take place to any extent, from none at all to a hundred per cent. That is, there is a complete series from the wholly ferrous condition to the wholly ferric condition (if there is enough hydroxyl in the original mineral). It is of course possible to divide such a series into two or more parts and call each part a mineral, but such divisions have no natural basis—they are purely arbitrary and artificical—and it seems much better to consider such a series as merely different conditions of one mineral.

Certain concrete cases may serve to illustrate these general principles.

Some phosphates contain hydroxyl and ferrous iron, but they are not well known and therefore little is known regarding oxidation in them. However, ludlamite, alluaudite, and triploidite illustrate the condition. Certain hydrous phosphates contain iron which is oxidized very easily, but it is not clear whether this is accomplished in the mineral or with destruction of the mineral. Such a condition is illustrated by vivianite and symplesite.

Biotite commonly contains both hydroxyl and ferrous iron, but it also contains so many other variables that the effects of oxidizing the iron are not yet well known. This is doubtless due in part to the presence in many biotite samples of ferric iron not derived from oxidation of ferrous iron, but a primary constituent which proxies for some aluminum.

In 1930 Barnes[2] proved that when common hornblende is changed to "basaltic hornblende" by heating, the change is due to loss of hydrogen

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[2] Barnes, V. E., *Am. Mineral.*, **15**, 393 (1930).

with accompanying oxidation of ferrous iron; that is, a hornblende originally having, for example, the formula $Ca_2Mg_2Fe_2''AlSi_7AlO_{22}(OH)_2$ becomes $Ca_2Mg_2Fe_2'''AlSi_7AlO_{24}$. Such a change occurs gradually and is accompanied by a gradual decrease of the extinction angle to 0°, a gradual increase of refringence and birefringence, and also in dispersion and in density, while the optic angle becomes about 60° and the color changes from green to brown. All these changes can be reversed, and the original condition obtained again, by reheating the mineral in hydrogen, which introduces the hydrogen once again and changes the iron from ferric to ferrous. The changes in optic properties caused by such oxidation of two atoms of ferrous iron in two end-members of the hornblende system are shown as obtained approximately by the author's recent study of calciferous amphiboles[3] in Figs. 1 and 2. The first figure shows the results of oxidation of iron in ferrotremolite $\{Ca_2Fe_5Si_8O_{22}(OH)_2\}$ and the second figure shows the same results for $NaCa_2Fe_5''Si_7AlO_{22}(OH)_2$ changing gradually to $NaCa_2Fe_3''Fe_2'''Si_7AlO_{24}$. Other end-members of hornblende may contain some Fe''' (proxying for Al) before any oxidation of ferrous iron occurs; in spite of this complication it is clear that oxidation produces very similar results in them.

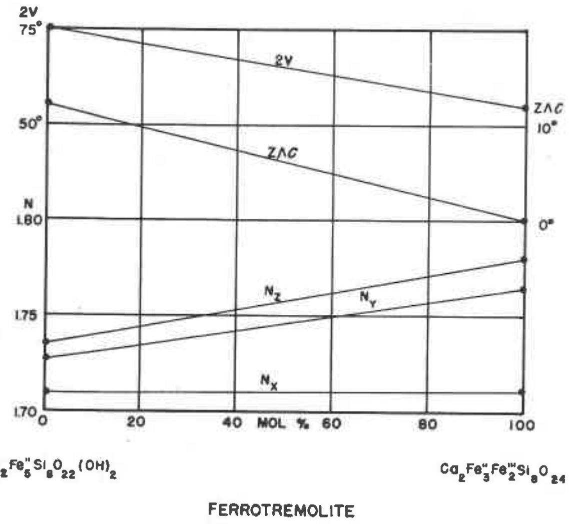

FIG. 1

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[3] Winchell, A. N., *Am. Mineral.*, **30**, 27 (1945).

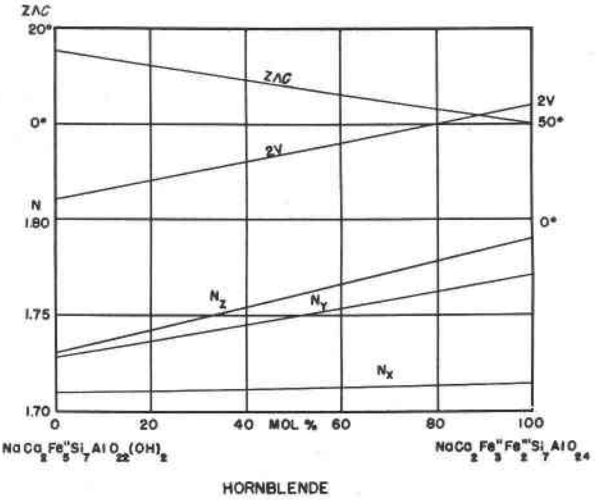

FIG. 2

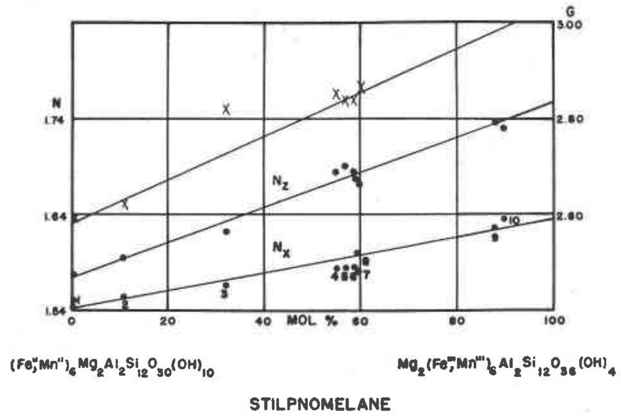

FIG. 3

Stilpnomelane is a rather rare "brittle mica" which varies in composition in many ways, but the greatest and most important variation is in the oxidation of the iron (and manganese). Disregarding other variations (since they are clearly minor in amount and in importance) the mineral varies from[4] about $(Fe'', Mn'')_6Mg_2Al_2Si_{12}O_{30}(OH)_{10}$ to about $Mg_2(Fe''',$

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[4] Analyses show about as much H_2O in Fe‴-rich stilpnomelane as in the Fe″-rich type, but Hutton (*Mineral. Mag.*, **25**, 172, 1938) found evidence that Fe‴-rich types contain less hydroxyl.

Mn''')$_6$Al$_2$Si$_{12}$O$_{36}$(OH)$_4$. The very considerable variations in optic properties corresponding with this variation in composition are shown[5] in Fig. 3.

Chlorite is a mineral which contains hydroxyl and may contain ferrous iron. The author considers[6] that so-called "leptochlorite" differs from ordinary chlorite only because its ferrous iron has been more or less oxidized to the ferric state. Dschang[7] has shown that such a change can be produced artificially. In general the change raises the indices of refraction and increases the birefringence; it may cause a change in the optic sign from positive to negative. The effects upon certain types of chlorite[6] are shown approximately in Fig. 4.

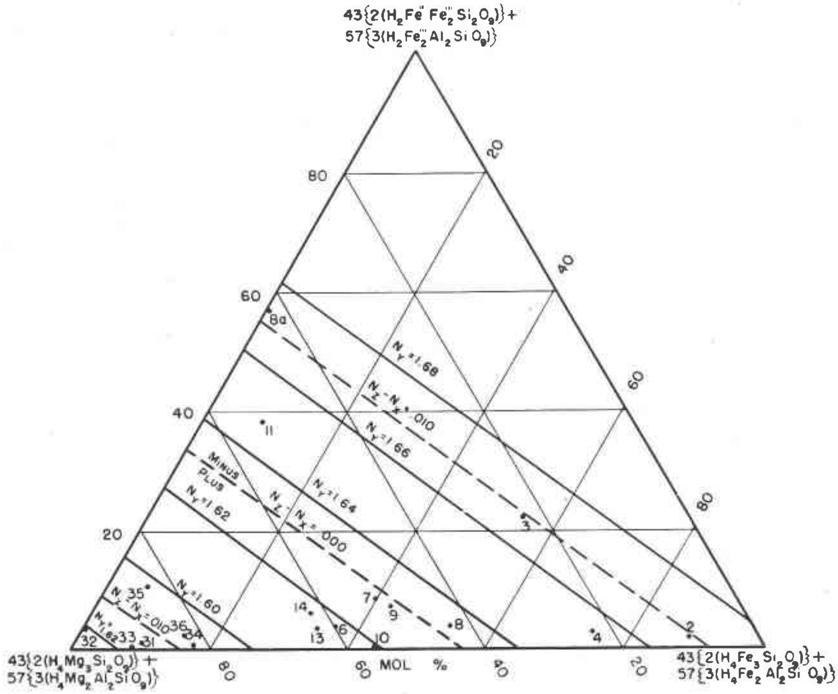

FIG. 4

Johnsen[8] proved that a crystal of sphene containing only 0.5 per cent of FeO changes from yellow to deep brown when the iron is oxidized by

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[5] Hutton (*loc. cit.*) based a similar diagram on weight percentage of divalent and trivalent bases.

[6] Winchell, A. N., *Am. Mineral.*, **21**, 642 (1936).

[7] Dschang, G. L., *Chem. Erde*, **6**, 416 (1931).

[8] Johnsen, A., *N. Jahrb. Mineral., Bl. Bd.*, **48**, 136 (1923).

heating in air and reverts to the original condition when next heated in hydrogen. This was doubtless due to the presence of a little hydroxyl in the original crystal.

In summary, it is evident that oxidation *of* minerals is accomplished by addition of oxygen and complete destruction of the original mineral, whereas oxidation *in* minerals is accomplished by loss of hydrogen but with no addition of oxygen and no destruction nor even any considerable change in the structure or properties of the original mineral.