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THE AMERICAN MINERALOGIST VOL. 49, JULY-AUGUST, 1964

INVESTIGATIONS OF LANDESITE

PAUL B. MOORE, *Dept. of Geophysical Sciences, University of Chicago, Chicago, Illinois.*

Landesite, a rare hydrated manganous-ferric phosphate, is an alteration product of reddingite which, in turn, is derived from the hydration and alkali-leaching of lithiophilite-triphylite at the Berry Quarry, Poland, Maine. The lithiophilite-triphylite material from this locality has a Mn:Fe ratio of approximately 3:1, and the alteration products represent the manganese side of the Mn-Fe series. Thus, reddingite and landesite also have Mn:Fe about 3:1.

The chemical analysis of landesite by Gonyer (1930) yielded the formula $\text{Fe}^{3+}_6\text{Mn}^{2+}_2(\text{PO}_4)_{16} \cdot 27\text{H}_2\text{O}$. There is a serious charge imbalance of 10 electrons, and somehow this remained unnoticed all these years. A quick glance suggests a very close relationship to reddingite, $(\text{Mn}, \text{Fe})_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ or even huréaulite, $\text{H}_2\text{Mn}_5(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$, except for the presence of ferric iron in landesite.

The writer, who is presently developing a general structural classification scheme for hydrated Fe-Mn phosphates, undertook single crystal studies of landesite in order to clarify its relationship to reddingite. A small ($0.1 \times 0.1 \times 0.2$ mm) fragment, dirty yellowish-brown in color, kindly supplied by Dr. D. J. Fisher, was selected for this study. The single crystal data (Table I) as well as powder data (Table II) agree very well with reddingite but show that subtle differences exist.

The powder film data were obtained from the same type materials using Fe/Mn radiation, 114.6 mm camera diameter, and NaF as internal standard. Relative intensities are visual estimates.

The optical data of Berman and Gonyer (1930) clearly show that Fe^{3+} is an integral part of the landesite formula. The best cleavage in landesite is {010} and was indexed to conform with space group *Pbcn*. The vibration normal to {010} has the index 1.735 for landesite in

TABLE I. UNIT CELL PARAMETERS OF LANDESITE AND REDDINGITE FROM
BERRY QUARRY, POLAND, MAINE
Mn:Fe approx. 3:1

Landesite		Reddingite	
	Orthorhombic <i>Pbcn</i> ¹		Orthorhombic <i>Pbcn</i> (Flachsbart, 1963) ¹
<i>a</i>	8.47 ± .03 Å		8.72 Å
<i>b</i>	9.43 ± .03		9.54
<i>c</i>	10.17 ± .04		10.08 (Palache <i>et al.</i> , 1951)
Vol.	813.3 Å ³		833.0 Å ³

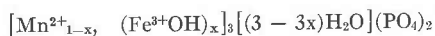
¹ Very weak reflections suggest a cell of lower symmetry (*Pb2n*).

contrast to 1.643 for reddingite. Furthermore, the sign of landesite is negative, and the sign of reddingite is positive.

A comparison of the cell volumes of Berry Quarry landesite and reddingite shows landesite to have the smaller volume. The principal change is the shrinkage along the *a*-axis which can be explained as the "hydroxylation" of an octahedrally coordinating water, the OH⁻ group being more tightly bound to the Fe³⁺ ion than H₂O to the Fe²⁺ ion. The writer believes the landesite-reddingite problem is another example of the common occurrence in hydrated Fe-Mn phosphates: concomitant charge balance of Fe³⁺ in oxidized Fe²⁺-Mn²⁺ phosphates by the "hydroxylation" of the octahedrally coordinating water without any significant change in crystal structure. Childrenite, vivianite, ludlamite, and huréaulite may be other examples.

Octahedral coordination seems to be the rule for Fe²⁺ and Mn²⁺ ions in hydrated orthophosphates (refer to the crystal structures of vivianite, ludlamite and reddingite) and the ligands are probably of the 3D²4S4P³ or 4S4P³4D² bond type (Kleinberg *et al.*, 1960). The corresponding oxidation of Fe²⁺ to Fe³⁺ simply results in the preservation of the ligand of bond type 3D²4S4P³ or 4S4P³4D² with an H₂O becoming an OH⁻ to satisfy the charge imbalance. Thus, for example, the ligand Fe²⁺(OH)₂(H₂O)₄, upon oxidation of the metal, can become Fe³⁺(OH)₃(H₂O)₃.

The landesite formula is better expressed in the following manner, remembering that in reddingite-type structures all the water contributes in octahedral coordination about Fe, Mn ions (Flachsbart, 1963).



in which, for type landesite, *x* is approximately 0.25.

TABLE II. POWER DATA OF LANDESITE AND REDDINGITE,
BERRY QUARRY, POLAND, MAINE

Landesite				Reddingite			
I/I ₀	d _{obs}	d _{calc}	hkl	I/I ₀	d _{obs}	d _{calc}	hkl
6	5.370	5.36	111	6	5.388	5.41	111
8	5.096	5.09	002	8	5.046	5.03	002
5	4.728	4.72	020	4	4.714	4.76	020
8	4.284	4.28	021	7	4.280	4.30	021
4	3.966	3.96	112	3	3.951	3.96	112
$\frac{1}{2}$	3.631	3.61	211				
4	3.464	3.46	022	4	3.443	3.46	022
10	3.207	3.20	122	10	3.204	3.21	122, 220
7	3.163	3.15	220				
5	3.090	3.08	212				
3	3.021	3.01	221	4	3.097	3.11	221, 212
				2	3.042		
2	2.956	2.99	113	3	2.966	2.97	113
3	2.836	2.84	131				
4	2.758	2.75	023	8	2.745	2.74	023
3	2.721	2.71	310				
8	2.630	2.62	123	7	2.662	2.63	123
				2	2.560		?
2	2.557	2.54	004	2	2.511	2.51	004
2	2.484	2.47	302				
2	2.448	2.45	231	3	2.471	2.48	231
4	2.400	2.39	312	6	2.423	2.43	312
1	2.363	2.36	321				
				3	2.346	2.34	114
5	2.227	2.24	024	6	2.222	2.22	024
1	2.190			4	2.179		
1	2.165			5	2.127		
4	2.132			1	2.070		
3	2.034			4	2.031		
3	1.952			4	1.965		

About 30 reflections of lower d-spacings, each having intensity less than 4.

The writer believes that the name, landesite, should be retained for the Fe³⁺-OH end member of the reddingite series with Mn:Fe greater than 1. Even better would be the name "ferri-reddingite" with the intention that the formal names be abandoned for all members of this series (Fe²⁺-Fe³⁺-Mn²⁺) in favor of "ferro-," "ferri-," and "mangano-" prefixes.

I wish to thank Dr. D. J. Fisher for use of the little type landesite available and Dr. P. H. Ribbe for reading the manuscript.

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THE AMERICAN MINERALOGIST, VOL. 49, JULY-AUGUST, 1964

OPTICAL EXTINCTION OF ANORTHITE AT HIGH TEMPERATURES

F. DONALD BLOSS, *Department of Geology, Southern Illinois University, Carbondale, Illinois.*

INTRODUCTION

Investigations by Brown *et al.* (1963) recently provided new insight on the sub-solidus phase relationships for crystals of anorthite compositions. Their *x*-ray photographs, taken of anorthite crystals at temperatures between 25° and 350° C., showed the *c*-reflections—that is, those for which $h+k$ is even whereas l is odd—to become increasingly diffuse and eventually disappear as 350° C. was approached. Thus a continuous and reversible structural transformation between 25° and 350° was demonstrated. Only in specimens quenched from temperatures in the range 1100°–1540° were structural stages comparable to those observed between 25° and 350° C. retained at room temperature, being closer to the 350° C. stage to the extent that the quench temperature approached 1540° C.

Using anorthite as an example, this present study reveals that transformations from one phase to another, as temperature is raised, may be determined relatively quickly by measuring the rate of change in the privileged directions of crystal sections as temperature is raised. Thus, for example, the change in value of the extinction angle, $[100]:\alpha'$, for (001) cleavage flakes of anorthite, as temperature is increased, offers further confirmation of a continuous structural transformation at about 350° and, moreover, indicates that a displacive transformation may also occur at about 800° C. The results from this present study indicate that a polarizing microscope used in combination with a heating stage may provide a ready means for detecting phase transformations at elevated temperatures. Details of the study follow.

METHOD AND APPARATUS

A high pressure mercury lamp (Zeiss HBO 200) was used as the light source for an ordinary polarizing microscope equipped with a Leitz