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ON THE VALIDITY OF CALDERITE

PETE J. DUNN
Department of Mineral Sciences, Smithsonian Institution, Washington, D.C. 20560, U.S.A.

ABSTRACT

A garnet sample from Otjosondu, Namibia (Southwest Africa) is re-examined and found to contain ~50 mol. % of the calderite component. The new data support older investigations and establish the legitimacy of calderite, ideally $Mn_3Fe^{3+}{}_2(SiO_4)_3$, as a species of the garnet group. The sample studied has a 11.81(1)Å, n_D 1.875(2) and D(obs.) 4.05 g/cm³. Microprobe analysis yields the empirical formula $(Mn_{3.92}Ca_{2.19})_{\Sigma 6.11}(Fe^{3+}{}_{2.07}Al_{1.74}Mg_{0.13}Ti_{0.03})_{\Sigma 3.97}(Si_{5.94}Al_{0.06})O_{24}$. The oxidation state of the iron was calculated to fit the valence requirements of garnets. *Ct* is proposed as an acronym for calderite.

SOMMAIRE

Au réexamen, un échantillon de grenat de Otjosondu (Namibie) s'avère contenir ~50% (mol.) du pôle *caldérite* [*ct*: $Mn_3Fe^{3+}{}_2(SiO_4)_3$], dont la validité comme membre de la famille des grenats est confirmée. Les mesures donnent a 11.81(1) Å, n_D 1.875(2) et D_{obs} 4.05. L'analyse à la microsonde conduit à la formule empirique $(Mn_{3.92}Ca_{2.19})_{\Sigma 6.11}(Fe^{3+}{}_{2.07}Al_{1.74}Mg_{0.13}Ti_{0.03})_{\Sigma 3.97}(Si_{5.94}Al_{0.06})O_{24}$. Le fer est considéré comme ferrique pour satisfaire à l'équilibre des charges.

(Traduit par la Rédaction)

INTRODUCTION

The name *calderite* was first given to a "siliceo iron and manganese rock" from Katkamsandi, northwest of Hazaribagh, in what is now the state of Bihar in western India, by Piddington (1851). The analysis was likely faulty and it was recognized as that of a garnet by Blandford & Söchting (1857). Calderite remained poorly defined for some years and was used by Mallet (1887) to describe both a "manganese-iron garnet" and a common andradite. In 1909 Fermor formally applied the name calderite to the theoretical end-member $Mn_3Fe^{3+}{}_2(SiO_4)_3$, which is the manganese analog of andradite, $Ca_3Fe^{3+}{}_2(SiO_4)_3$, and the ferric iron analog of spessartine, $Mn_3Al_2(SiO_4)_3$. This nomenclature was continued by Fermor (1927) in his investigation of some Indian garnets.

A second occurrence of calderite was noted by de Villiers (1951), and the material was subsequently re-examined by Vermass (1952). In a third description, Klein (1966) described some calderites from the Wabush iron formation in southwestern Labrador. In spite of these descriptions, calderite remains unrecognized in most reference works as a legitimate end-member of the garnet group.

CHEMISTRY

The sample studied was analyzed with an ARL-SEMQ electron microprobe using an operating voltage of 15 kV and a beam current of 0.15 μA. The data were corrected for background, backscatter absorption and fluorescence using Bence–Albee factors. Standards used were a magnesian ferroan grossular for aluminum and silicon, manganite for manganese, hornblende for magnesium, calcium, iron and titanium, and chromite for chromium. The resultant analysis is presented in Table 1. Iron was determined as total iron, and the oxidation state of the iron was calculated to fit the known valence requirements of garnets, using the deficiency of aluminum as an indicator of the amount of iron present in the ferric state.

Examination and analysis of a number of specimens labeled *calderite* in the Smithsonian collections and the collections of the British Museum (N. H.) indicated that most of these specimens are ferroan and magnesian andradites. They are hosts for abundant inclusions of ferroan diopside and magnesian hedenbergite, which likely contributed to incorrect wet-chemical analyses.

DISCUSSION

Only one of the specimens studied, BM 1951-21 from Otjosondu, Namibia, is germane to this discussion because of its high manganese and iron content. The sample is dark reddish brown, with many stringers of pyrolusite and other manganese oxides, and is chemically

TABLE 1. CHEMICAL ANALYSES OF CALDERITE

	1.	2.	3.	4.
SiO_2	35.16	34.56	5.942	5.984
TiO_2	0.28		0.036	
Al_2O_3	9.04	4.72	1.801	0.963
Fe_2O_3*	16.27	22.96	2.069	2.992
FeO	0.00		0.000	
MgO	0.50	0.56	0.126	0.145
CaO	12.12	14.60	2.195	2.709
MnO	27.38	22.12	3.919	3.244
Total	100.75	99.52		

1. BM 1951-21, microprobe analysis.
2. BM 1951-21, from Vermass (1952)
3. number of ions, based on 24 oxygens, for #1.
4. number of ions, based on 24 oxygens, for #2.

Accuracy of data for analysis #1: ±2% of amount present.

*- Iron determined as total iron and calculated to fill deficiency for 3+ ions in the garnet structure.

homogeneous. This sample, given to the British Museum (N. H.) by de Villiers, is the same sample analyzed by C. F. J. de Walt in de Villiers (1951) and reanalyzed by Vermass (1952) as his garnet #1.

The physical determinations of the present study [*a* 11.81(1)Å, n_D 1.875(2), *D* (obs.) 5.05 g/cm³] are in good agreement with those of Vermass (1952): *a* 11.819Å, n_D 1.872, *D* (obs.) 4.081 g/cm³. Application of the Gladstone–Dale relationship (Mandarino 1976) to this garnet yields a K_C value of 0.215 determined from the chemical analysis, compared with a K_P value of 0.216 determined from physical properties. The compatibility index, $(1.000\text{-}K_P/K_C)$ (Mandarino 1979) is 0.005, indicating superior compatibility of the data.

An examination of the analysis of sample BM 1951-21 in Table 1 indicates it is slightly deficient in 3+ ions. This deficiency may be due to experimental error or the presence of some manganese as Mn^{3+}. The empirical formula of this specimen, calculated on the basis of 24 oxygen atoms, is $(Mn_{3.92}Ca_{2.19})_{\Sigma 6.11}(Fe^{3+}_{2.07}Al_{1.74}Mg_{0.13}Ti_{0.03})_{\Sigma 3.97}(Si_{5.94}Al_{0.06})O_{24}$. The sample clearly does not fall within the composition range of the recognized garnet species; it is a legitimate calderite and conforms to the general formula for the end-member, $Mn_3Fe^{3+}_2(SiO_4)_3$. The observations of Vermass (1952) are confirmed; although the composition of this garnet could be expressed as *Spessartine*$_{44}$*Andradite*$_{36}$*Calderite*$_{20}$, this calculation only serves to point out that this garnet cannot be assigned to the composition range of the garnet group without the presence of the calderite component.

Considering that the calderite component must be present, at least in part, to account for the uncommon composition of this garnet, it is much simpler to calculate the composition in terms of the three dominant end-members (calderite, spessartine and grossular) as *Calderite*$_{51}$ *Grossular*$_{36}$*Spessartine*$_{13}$.

The preceding data relate to the Otjosondu sample only. Klein (1966) published a description of calderite samples from the Wabush iron-formation in Labrador. His samples occur in two assemblages: (1) an aegirine–rhodonite–hematite–rhodochrosite assemblage, and (2) a quartz–hematite–rhodonite–kutnahorite–calderite rock. Chemical analyses of these samples yielded $(Mn_{2.20}Ca_{0.82})$ $(Fe^{3+}_{2.02})$ $(SiO_4)_{3.00}$ for sample (1) and $(Mn_{1.85}Ca_{1.16})$ $(Fe^{3+}_{2.02})$ $(SiO_4)_{3.00}$ for sample (2). Klein's samples are very low in aluminum (less than 0.3% estimated) and are very clearly legitimate calderites and closer to the end-member composition than the aluminous Otjosondu sample described here.

In summary, calderite is a legitimate and valid end-member of the garnet group. *Ct* is proposed as an acronym for calderite inasmuch as the other possibilities, Ca, Cl, Cd, Ce and Cr, are all symbols of chemical elements.

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