GEM ANDRADITE GARNETS

By Carol M. Stockton and D. Vincent Manson

Andradite, the rarest of the five well-known gem garnet species, is examined and characterized with respect to refractive index, specific gravity, absorption spectrum, color, and chemical composition. These properties are measured and specifically tabulated for 21 gem andradites (20 green and one yellow). From the narrow ranges of refractive index (1.880–1.883), specific gravity (3.80–3.88), and chemical composition (less than 3% of components other than andradite in any of the specimens examined) that were observed, it is apparent that the gem-quality andradites are chemically distinct from other types of gem garnets and that these stones are easy to distinguish by means of color coupled with refractive index.

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As part of our continuing study of gem garnets, the species andradite should present few difficulties in characterization and identification. Three varieties have been recognized by gemologists: melanite, topazolite, and demantoid. Melanite, which is black, will not be discussed here because it is opaque and has historically, to our knowledge, been used as a gem only for mourning jewelry. Topazolite, a term that has been challenged as being too similar to that of the gem species topaz, is a greenish yellow to yellow-brown andradite that only occasionally occurs in crystals large enough to be faceted. Demantoid, the yellowish green to green variety (figure 1), is the most important of the three for the jeweler-gemologist and is the principal focus of the study reported here.

Pure andradite ($Ca_3Fe_2Si_3O_{12}$) has a refractive index of 1.886 (McConnell, 1964) and a specific gravity of 3.859 (Skinner, 1956). Gemological references cite ranges as narrow as 1.888 to 1.889 for refractive index and 3.82 to 3.85 for specific gravity (Webster, 1975) and as broad as 1.855 to 1.895 and 3.81 to 3.87, respectively (Liddicoat, 1981). Demantoid has been observed to exhibit a visible light spectrum that has a very strong absorption band centered around 443 nm, which may appear as a cutoff, and, in the case of finer green stones, two bands around 622 nm and 640 nm as well as a pair of bands between 693 and 701 nm (Anderson and Payne, 1955). Liddicoat (1981) and Webster (1975) both support these observations. Anderson and Payne attributed the 443 nm band to Fe^{3+} and the remaining four bands to Cr^{3+}.

Two distinct characteristics of demantoid are usually used as visual indicators in identification. One is the very strong dispersion (0.057), which can be observed in almost any cut stone. The other is the frequent presence of "horsetail" inclusions (figure 2) of byssolite fibers (Gübelin, 1974). These inclusions are so unique and characteristic

that demantoid is frequently cut so as to position them directly beneath the table of a stone where they are unmistakably visible.

DATA COLLECTION

Because of the rarity of gem-quality andradites, we were able to compile a collection of only 21 samples: one brownish yellow stone and 20 green ones, of which 10 were from a single parcel. We attempted to add variety by borrowing stones, but only one specimen (#L-1) among those available to us was of a type not already represented by stones from GIA's reference collection. Moreover, reliable information on the origins of gems is exceedingly scarce (as compared, for instance, to collectible mineral specimens); among the stones studied here, only the locality of the brownish yellow specimen from California is known for certain.

Each stone was measured for refractive index, specific gravity, absorption spectrum, color, and chemical composition. The instruments and techniques employed for data collection were the same as those used in the previous portions of the garnet study and described in detail in our initial paper in this series (Manson and Stockton, 1981). However, because the microprobe system we use for quantitative chemical analyses reports all iron as Fe^{2+} while the iron in andradites is present principally as Fe^{3+}, mathematical conversion was necessary to correct the appropriate percentages. Any error in the determination of Fe^{2+} by the microprobe is compounded by this calculation, so we performed chemical analyses four times for each stone and averaged the results in an effort to increase the accuracy of the original figures. The data are summarized in table 1.

DISCUSSION OF DATA

Physical and Optical Properties. The ranges of refractive index and specific gravity that we obtained for our 21 andradites are quite narrow in comparison to other types of garnets: 1.880–1.883 and 3.80–3.88, respectively. The refractive indices that we observed fall within the range cited by Liddicoat (1981) and below that of Webster (1975), as discussed above. The specific gravities for our specimens define a somewhat broader range than those proposed by the aforementioned sources. The often highly included nature of even gem-quality andradite would be sufficient to account for considerable variability in this property.

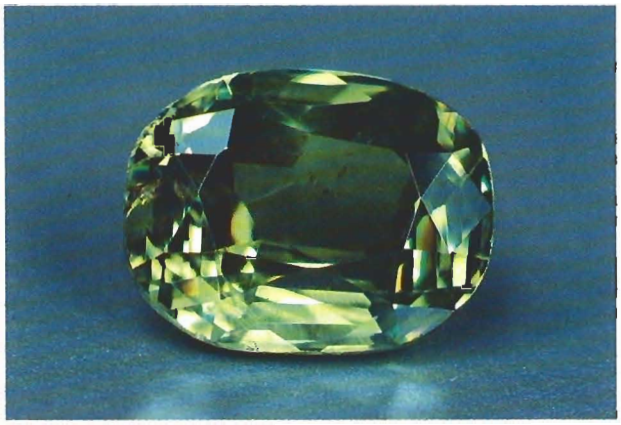
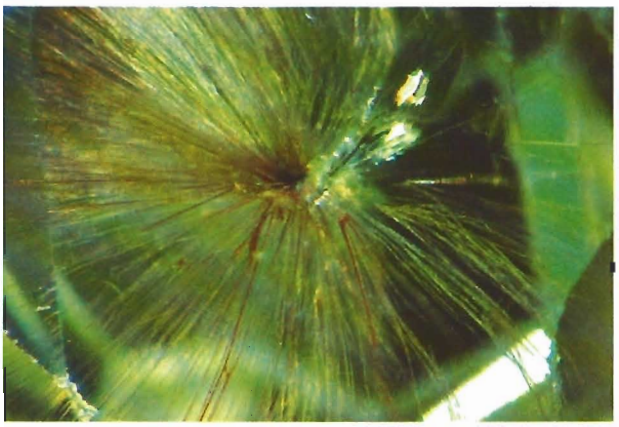


Figure 1. Andradite garnet, gem variety demantoid (GIA no. L-1).

Chemistry. It is evident from table 1 that there is very little variability in chemical composition among the andradites that we examined, especially when compared to other types of garnets. Moreover, this lack of deviation is reflected in the very narrow ranges observed for refractive indices and specific gravities. Greater compositional variation does occur in non-gem-quality andradites (Deer et al., 1963) to the extent that they appear to continuously grade into grossular. However, to our knowledge no gem-quality garnets with these intermediate compositions have been observed.

An examination of the totals in table 1 for oxide and end-member compositions reveals that our method of calculating garnet end members does not account for the oxides in andradites as well as it has for other types of garnets (Manson and Stockton, 1981). Comparison of figure 3 with

Figure 2. "Horsetail"-type inclusion in a demantoid andradite. Magnified 50×.



the histogram in our first article on garnets (figure 2, op. cit.) will clearly confirm this difference. The deficiency appears to be in cations that occupy the octahedral site (represented by Y in the garnet formula $X_3Y_2Z_3O_{12}$) leaving an excess of cations for the dodecahedral (X) and tetrahedral (Z) sites, especially calcium and silicon. This may be due to the possibility that andradite does not behave according to the ideal garnet formula employed by our end-member calculation scheme. Another likely explanation, especially evident in the large-scale conversion of FeO to Fe_2O_3 necessary for andradites, involves the presence of different oxidation states that cannot be distinguished with the microprobe (Huggins et al., 1977; Burns, 1981). In addition, there may be minor water content—fairly common in andradites (Deer et al., 1963)—that also cannot be detected with the microprobe.

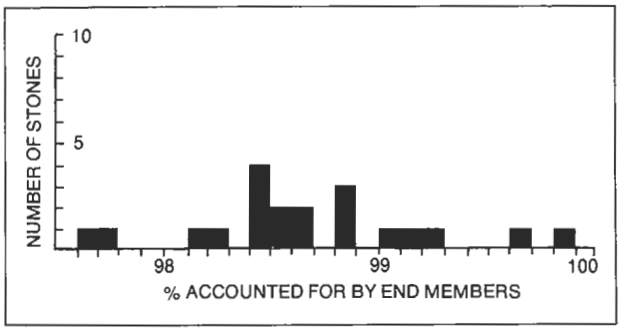


Figure 3. Histogram illustrating the percentages of oxides in the 21 andradites that are accounted for by end members.

It is interesting to note the low accountability that occurred with the one brownish yellow stone (#11648) that we examined.

TABLE 1. Physical, optical, and chemical data for 21 andradites from various localities.[a]

Physical, optical, and chemical properties	Italy (2491)	(2952B)	(13132)	(6672C)	(6672D)	(13234)	(13254)	(6672A)	(13163A)
Refractive index	1.881	1.881	1.883	1.880	1.880	1.881	1.881	1.881	1.880
Specific gravity	3.85	3.88	3.86	3.85	3.88	3.85	3.88	3.85	3.86
ColorMaster coordinates	A-18/34/01	A-24/65/05	A-19/54/05	B-45/85/03	A-15/30/01	B-36/72/02	B-46/100/05	A-25/65/05	A-17/52/03
CIE x/y coordinates	0.446/0.482	0.338/0.478	0.373/0.470	0.454/0.484	0.437/0.486	0.443/0.499	0.433/0.487	0.393/0.475	0.382/0.502
GIA color terminology[b]	YG 3/4	yG 2/2	syG 2/2	YG 4/4	YG 3/3	YG 4/4	YG 3/3	yG 2/2	yG 3/3
Oxide composition[c]									
SiO_2	35.33	35.83	35.70	35.39	35.27	35.61	35.47	35.43	35.59
Al_2O_3	0.10	0	0	0	0	0	0	0	0
Fe_2O_3[d]	30.56	30.97	31.35	31.09	30.68	31.01	31.07	31.26	31.12
Cr_2O_3	<0.05	<0.05	<0.05	<0.05	0.06	<0.05	<0.05	<0.05	0.10
Ti_2O_3[d]	0.09	0.03	<0.02	0.05	0.09	<0.02	<0.02	<0.02	<0.02
MgO	0.24	<0.05	<0.05	<0.05	0.07	0.12	0.11	0.07	0.07
CaO	33.66	33.45	33.49	33.44	33.28	33.48	33.41	33.58	33.35
MnO	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Total	100.08	100.43	100.71	100.12	99.50	100.34	100.18	100.45	100.30
End-member composition[e]									
Schorlomite	0.36	0.11	<0.07	0.18	0.32	<0.07	<0.07	0.07	<0.07
Andradite	97.24	98.56	99.67	98.93	97.71	98.58	98.79	99.46	98.93
Uvarovite	<0.16	<0.16	<0.16	<0.16	0.20	<0.16	<0.16	<0.16	0.33
Total	97.76	98.83	99.90	98.23	98.25	98.81	99.02	99.69	99.33
Spectral absorption bands (nm)	475	446	445	456	457	450	451	446	447
	565	574	571	567	571	571	573	573	574
	621	621	622	620	624	622	625	624	622
	738	738	—	—	—	—	740	740	740

[a] *The GIA catalogue number for each stone is indicated in parentheses.*
[b] *Color terminology refers to "hue tone/saturation." The symbols are interpreted as follows:*
Hue: s = slightly; o = orangy; y = yellowish; Y = yellow; G = green
Tone: 2 = very light; 3 = light; 4 = medium light
Saturation: 2 = slightly grayish hue; 3 = very slightly grayish hue; 4 = hue

Another point of interest is that some of the stones apparently are not homogeneous in composition, especially with regard to chromium. The Cr_2O_3 content of one stone was determined in four separate analyses to be 0.18, 0.26, 0.13, and 0.05 weight percent. For comparison, the four analyses of another stone revealed 0.08, 0.06, 0.07, and 0.06 weight percentages of Cr_2O_3.

Color. The range of colors of gem andradite is fairly narrow and, with the exception of the rare and very desirable vivid green, is well represented by the stones we examined (figure 4). Consequently, the distribution of the color coordinates for these stones in the CIE color graph occupies a very small region (figure 5) in comparison to the broad color variability seen in most types of garnets. We did not observe color zoning in any of our stones, even in those with chemical analyses that suggested nonhomogeneous distribution of potentially color-influencing elements. Nor could we correlate the small amounts of Cr_2O_3 measured in these stones with variations in hue, since the quantities in many of the stones approached the limits of detection of the microprobe. In most cases, therefore, our figures for chromium incorporate a relatively high level of uncertainty.

Manganese and titanium have also been associated with color origin in andradites. The exact role of the latter has been the subject of considerable debate among mineralogists (Howie and Woolley, 1968; Moore and White, 1972; Manning and Harris, 1970; Huggins et al., 1977). The low levels of titanium present in the stones we analyzed could not be measured with sufficient accuracy to contribute toward clarifying the signifi-

			USSR							San Benito Co., Calif.	Unknown
(13163B)	(13163C)	(13163D)	(13163E)	(13163F)	(13163G)	(13163H)	(13163I)	(13163J)	(13103)	(11648)	(L-1)
1.880	1.880	1.881	1.881	1.880	1.882	1.882	1.881	1.883	1.880	1.881	1.881
3.87	3.84	3.88	3.84	3.83	3.86	3.87	3.83	3.83	3.81	3.80	3.87
A-20/50/03	A-17/50/02	A-18/52/04	A-19/58/04	A-20/57/05	A-17/52/02	A-20/57/03	A-21/52/04	A-24/65/05	A-28/64/05	B-83/96/01	A-18/56/02
0.401/0.487	0.392/0.517	0.381/0.482	0.378/0.490	0.377/0.473	0.385/0.517	0.391/0.495	0.392/0.469	0.388/0.478	0.407/0.465	0.528/0.444	0.388/0.520
YG 3/3	yG 3/3	yG 3/2	syG 3/3	syG 3/2	yG 3/4	yG 3/3	YG 3/2	yG 2/2	YG 2/2	soY 3/4	yG 3/4
35.46	35.66	35.53	35.51	35.63	35.62	35.87	35.72	35.72	35.27	35.56	35.40
0	0	0	0	0	0	0	0	0	0	0	0
30.74	30.93	30.87	31.13	30.83	31.02	31.22	31.10	31.08	31.14	30.52	30.99
0.16	<0.05	0.18	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.07
<0.02	0.04	0.03	<0.02	<0.02	0.03	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
<0.05	<0.05	0.06	<0.05	0.07	0.09	<0.05	<0.05	<0.05	<0.05	<0.05	0.09
33.37	33.38	33.46	33.50	33.38	33.38	33.42	33.62	33.52	33.51	33.29	33.55
<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.07	<0.05
99.85	100.16	100.18	100.31	100.03	100.24	100.68	100.61	100.49	100.09	99.56	100.17
<0.07	0.14	0.11	<0.07	<0.07	0.11	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07
97.73	98.44	98.25	98.96	98.01	98.60	99.25	98.86	98.79	99.00	97.02	98.50
0.53	<0.16	0.59	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	0.23
98.33	98.74	98.95	99.19	98.24	98.87	99.48	99.09	99.02	99.90	99.23	98.80
446	449	444	446	447	448	447	446	448	446	497	447
576	—	572	573	572	573	573	573	570	572	—	571
619	622	624	622	621	620	623	624	632	623	616	626
740	—	737	—	738	738	743	738	—	740	738	—

[c] *For a discussion of accuracy, see Appendix. Oxide figures are given as weight percentages.*
[d] *All FeO and TiO_2 were converted to Fe_2O_3 and Ti_2O_3 in accordance with the requirements of stoichiometry.*
[e] *$Mn_3V_2Si_3O_{12}$, knorringite, spessartine, grossular, and almandine were also considered by our end-member calculation program, but were all eliminated in the process due to the absence of the necessary oxides.*

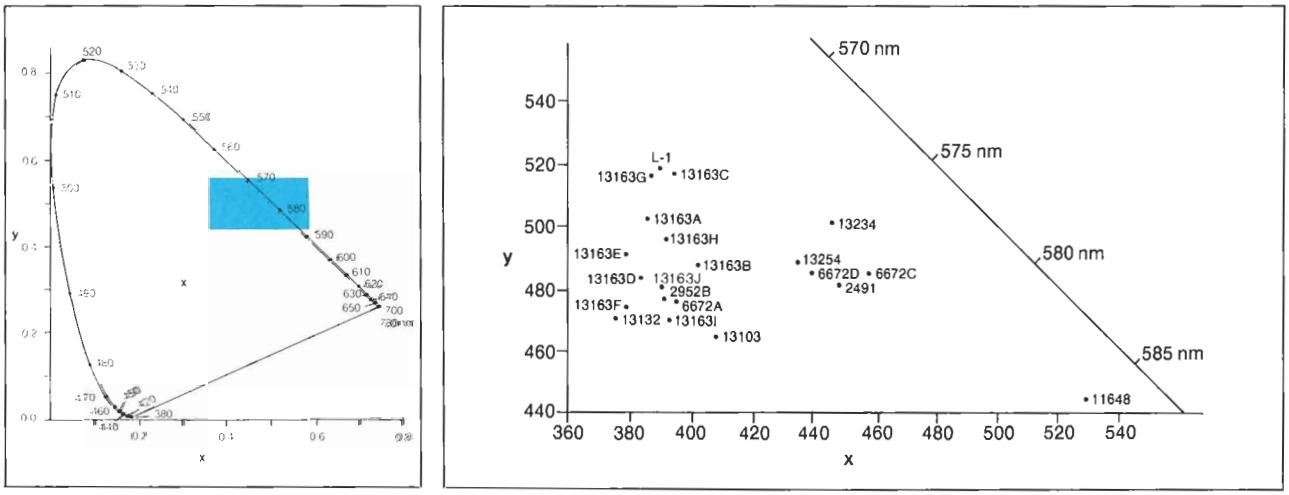
Figure 4. A selection of stones from the collection of andradite garnets used in this study which illustrates the ranges of colors of the stones examined. (From left to right, GIA nos. 11648, 2491, L-1, 13254, and 2952B.)

cance of titanium in andradites, but the possible effect of this element must not be ruled out. The presence of manganese in andradites has been documented in association with dark yellowish or reddish hues (Vermaas, 1952). Minor MnO content was detected in the one yellow-brown andradite that we analyzed, but this information is not sufficient to support any conclusions about the effects of manganese on the color of andradites.

Finally, the effects of different valence states and site occupancies of iron must be considered as a possible cause of color variation. There is evidence in the literature (Huggins et al., 1977; Schwartz et al., 1980; Burns, 1981) that iron, especially in the presence of titanium as in garnets of the andradite-schorlomite series, can be present in both divalent and trivalent states and can occupy sites other than those normally associated with those states. While these studies do not yet correlate such a distribution of iron with specific color effects, they do identify that absorption of visible light and associated variations in color result from such relationships (Marfunin, 1979; Burns, 1981).

Spectrum. With the spectrophotometer, three absorption bands could usually be discerned in the visible light range: at approximately 446 nm, 573 nm, and 620 nm (figure 6). The latter two bands may overlap considerably and at times appear as a single broad absorption, especially in the yellowish green to yellow-brown stones. In this form, they are centered around 600 nm and are referred

Figure 5. Left, the CIE chromaticity diagram with an indication of the region (shaded area) reproduced at right; x indicates the coordinates for colorless or neutral gray. Right, the yellow-green to yellow region of the CIE chromaticity diagram with positions for the 21 andradites plotted according to their x-y color coordinates.



to in the mineralogical literature as associated with the presence of Fe^{3+} in the octahedral site (Slack and Chrenko, 1971; Moore and White, 1972). These references assign the same significance to the 446 nm band. Only one source (Amthauer, 1976) refers to a single band near 621 nm and attributes it to Cr^{3+}, but no source has cited the 573 band separately. These bands may also reflect the presence of Cr^{3+}, which appears in grossulars as bands around 427 nm and 611 nm (Amthauer, 1976), but the overlap of such Cr^{3+} bands with those of Fe^{3+} in andradite would make it difficult to separate their respective influences on color. In addition, we observed a well-defined band in the near-infrared region, around 740 nm, in over half of the andradites. As yet, we have found no reference to this band in either the mineralogical or gemological literature, nor any correlation with chemical composition in the stones in which it was observed.

With the hand spectroscope, the absorption spectrum reveals a strong band at 430 to 445 nm, which at time appears as a cutoff at 445 nm, and a vague, broad band centered at approximately 590 nm (figure 7). The latter, it should be noted, is not mentioned in the gemological sources we cited in the introduction to this article. We were unable to confirm the paired bands associated with rich green color and/or Cr^{3+} mentioned by these same sources (Anderson and Payne, 1953–1957; see also those cited in the introduction to this article), since they were not present in the spectra of any of the stones we examined, probably because none of our specimens were of the finest green color associated with demantoids. We would welcome the opportunity to examine such material if it were made available to us.

Figure 6. Representative spectral curve of a demantoid (no. 131633) as observed with the spectrophotometer. Principal absorption and transmission features are labeled with their specific wavelengths. All or most of these features were observed in all the demantoids examined.

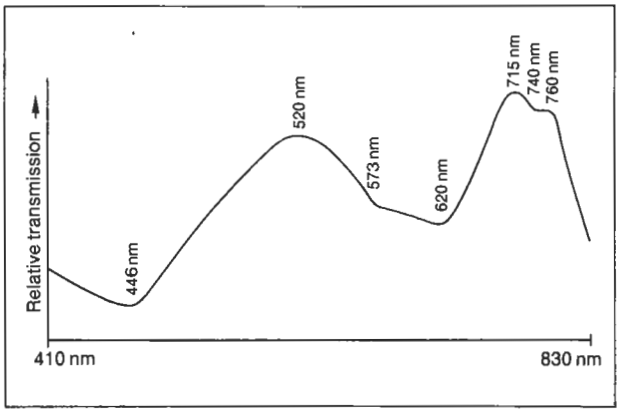
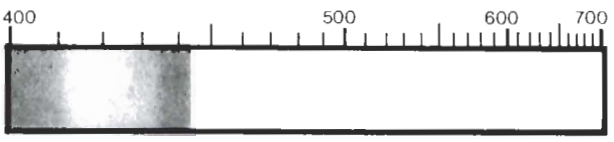


Figure 7. The same absorption spectrum illustrated in figure 6 as it is seen with the hand spectroscope. The absorption features in the blue region often appear as complete absorption below approximately 440 nm to 445 nm.



CONCLUSIONS

As in our previous studies on garnets, the definition of varieties according to characteristic spectra and corresponding color-causing elements has proved to be complex. We were able to detect no correlation between color, spectral absorption bands, and the amount of Cr_2O_3 present in the stones we examined. However, we have no reason to question the existence of absorption bands associated with high Cr_2O_3 content in more intensely green demantoids. The influences of titanium and manganese on the variability of color among gem andradites are still very questionable. While Fe^{3+} in the octahedral site is responsible for the yellow-green color of most gem andradites, iron in other valence states and in other sites in the garnet structure may also contribute to variation.

The high proportion of the andradite component in gem andradites provides ease in clearly defining the gem species associated with this end member of the garnet group. It is characterized by very little variability in chemical composition and in optical and physical properties in comparison with other types of garnets. Members of the gem andradite species can be easily distinguished by means of their high refractive index (1.880–1.883) in conjunction with color. No other type of gem garnet that has a refractive index over 1.80 occurs in green to yellow-brown hues. The precise definition of the gem varieties of andradite will be discussed in our concluding article on the gem garnets as a whole.

APPENDIX

The accuracy of our chemical data is affected principally by the amount of chemical inhomogeneity in our samples and by the variability and bias inherent in the techniques employed in chemical analysis. Aside from the problem of inhomogeneity, the accuracy of our microprobe data can be assessed through an examination of the variation among selected analyses of a well-known standard material, the McGetchin garnet (McGetchin, 1968), which we analyze each time we place a set of specimens in the instrument. Table 2 provides ranges, averages, and standard deviations for 25 microprobe analyses of the McGetchin garnet collected over a two-year period in conjunction with the analyses of the specimens described in this article.

TABLE 2. Ranges, averages, and standard deviations for 25 microprobe analyses of the McGetchin garnet over a two-year period.

Oxide	Range of wt %	Average of wt %	Standard deviation (%)
SiO_2	40.45–42.30	41.45	± 1.06
TiO_2	0.12– 0.20	0.16	±13.79
Al_2O_3	21.62–22.94	22.35	± 1.59
Cr_2O_3	1.32– 1.44	1.38	±18.16
V_2O_3	0– 0.08	0.03	±88.33
MgO	19.60–20.42	20.04	± 1.16
CaO	4.47– 4.69	4.63	± 1.12
MnO	0.29– 0.50	0.37	±18.94
FeO	8.99– 9.55	9.23	± 1.48

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