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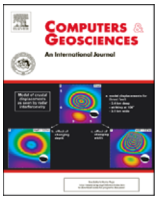

An Excel spreadsheet to recast analyses of garnet into end-member components, and a synopsis of the crystal chemistry of natural silicate garnets ☆

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ABSTRACT

A Microsoft Excel spreadsheet has been programmed that allows users to calculate with ease the molar proportions of garnet end-members from chemical analyses. Recent advances in the understanding of the crystal chemistry of natural garnets, especially of the Ti-bearing garnets, are used to evaluate 29 end-members (15 species and 14 hypothetical end-members) for each analysis. The amounts of Fe^{2+} and Fe^{3+} (and Mn^{3+}, if necessary) are calculated by stoichiometric constraints if these quantities have not been measured. The input data can include: SiO_2, TiO_2, ZrO_2, SnO_2, Y_2O_3, Al_2O_3, Sc_2O_3, Cr_2O_3, V_2O_3, FeO, Fe_2O_3, MnO, MgO, CaO, Na_2O, H_2O+ and F. The spreadsheet can be used with large data sets (up to 100 analyses at a time), and is accompanied by results calculated for 470 garnet analyses taken from the literature. The spreadsheet employs a simple scoring algorithm to measure the quality of a garnet analysis. The propagation of error from the input chemical data to the calculation of end-member proportions is also discussed briefly.

1. Introduction

Natural garnets are an important group of orthosilicate minerals that occur in a wide variety of geologic environments (Deer et al., 1997), and whose chemical compositions are of particular significance in geothermobarometry (e.g., Spear, 1993). The general formula of anhydrous garnet may be expressed as $\{X_3\}[Y_2](Z_3)\phi_{12}$, where X, Y and Z are cations, { } indicates eightfold coordination of the cations, [ ] denotes octahedral coordination, ( ) signifies tetrahedral coordination and ϕ corresponds to the anion site. The garnet crystal structure has been described as one of considerable chemical compliance (Hawthorne, 1981): it can accommodate a wide variety of elements, with the result that a large number of synthetic compounds adopt this structure type (Geller, 1967; Hawthorne, 1981). In natural systems, specimens of garnet exhibit extensive solid solution; consequently, their chemical compositions are often expressed in terms of the molar proportions of end-member components (Hawthorne, 2002). Although there are 15 cubic mineral species in the garnet group (Mandarino and Back, 2004), the chemical compositions of natural garnets commonly cannot be fully expressed in terms of these species. Hypothetical end-members (those end-members that have not been shown to form individually a majority of any natural garnet specimen, and thus do not warrant the status of mineral species) are also required to describe the chemical complexity inherent in many natural specimens of garnet.

Several procedures have been presented for the recalculation of analyses of garnet into molar proportions of end-member components. Rickwood (1968) presented a thorough discussion of the difficulties inherent in recasting garnet analyses, including a discussion of which end-members are appropriate and the influence of the

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☆ Code available from server at http://www.iamg.org/CGEditor/index.htm.

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calculation sequence upon the results. The recursive procedure of Rickwood (1968), which uses 19 end-members, was programmed into an early mainframe computer and is the foundation of the BASIC program of Knowles (1987), the Lotus 1-2-3 spreadsheet of Friberg (1989) and the linear programming method of Yang (1991). Although Rickwood's procedure has been widely used (cf. the compilation of Deer et al., 1997), it was criticized by Muhling and Griffin (1991), largely on the basis of its inappropriate treatment of titanium. The latter authors presented a QuickBASIC program that makes use of 16 end-members, and which produces results that differ from those of Rickwood (1968), most notably in the treatment of chromium, iron and titanium.

The Excel spreadsheet described here takes advantage of recent advances in the understanding of the crystal chemistry of natural garnets, especially of the Ti-bearing garnets (Chakhmouradian and McCammon, 2005; Henmi et al., 1995). It is intended to be used with chemical compositional data, rather than with the results of structure refinement or spectroscopic experiments. In order to accommodate the range of major-element compositions observed in nature, 29 possible end-members are evaluated for each analysis (15 mineral species and 14 hypothetical end-members). If the amounts of FeO and Fe_2O_3 have not been measured, stoichiometric constraints are applied to try to achieve charge balance; Mn^{3+} is calculated only for compositions that cannot charge balance with Fe^{3+} alone. Care was taken to ensure that, in so far as is possible, the results are in substantial agreement with those generated by the widely adopted procedure of Rickwood (1968), but with the advantage of a more realistic set of end-members, and the ability to accept a wider range of composition. The spreadsheet can be used with large data sets (up to 100 analyses at a time), and is accompanied by results calculated for 470 garnet analyses from both the recent literature and from Deer et al. (1997). The Microsoft program Excel was selected for this work because of its wide distribution and its ease of use.

2. Crystal chemistry

2.1. Chemical composition

The chemical compositions of natural silicate garnets are dominated by the following elements (listed in order of increasing atomic number): H, O, F, Na, Mg, Al, Si, Ca, Sc, Ti, V, Cr, Mn, Fe, Y, Zr and Sn (Amthauer et al., 1979; Chakhmouradian et al., 2008; Deer et al., 1997; Galuskina et al., 2005). Conventionally, the cations are expressed as oxides in percent by weight. Several other elements are reported only occasionally and only in low concentrations: Li, P, S, Cl, K, Ni, Zn, As, Sr, Nb, Te, Ba, REE, Hf, W and Th. These minor elements are not considered further as they do not normally contribute significantly to the compositions of natural silicate garnets. The non-silicate minerals that are isostructural with the garnet group: berzeliite, $\{Ca_2Na\}[Mg_2](As_3)O_{12}$ (Bubeck and Machatschki, 1935); cryolithionite, $\{Na_3\}[Al_2](Li_3)F_{12}$ (Menzer, 1927); manganberzeliite, $\{Ca_2Na\}[Mn_2](As_3)O_{12}$ (Ito, 1968); palenzonaite, $\{Ca_2Na\}[Mn_2](V_3)O_{12}$ (Basso, 1987); schäferite, $\{Ca_2Na\}[Mg_2](V_3)O_{12}$ (Krause et al., 1999); and yafsoanite, $\{Ca_3\}[Te_2](Zn_3)O_{12}$ (Jarosch and Zemann, 1989) are rare and have not been demonstrated to show extensive solid solution toward the silicate garnets, and are therefore disregarded for the purposes of this work.

2.2. General valence states

The formal valence states of most of the main constituent elements are invariable in the garnet structure: H^+, O^{2-}, F^-, Na^+, Mg^{2+}, Al^{3+}, Si^{4+}, Ca^{2+}, Sc^{3+}, Cr^{3+}, Y^{3+}, Zr^{4+} and Sn^{4+}. However, at least in principle, the first-row transition elements V, Mn, Fe and Ti can adopt two (or more) valence states. In practice, despite the existence of such rare vanadate minerals as palenzonaite, $\{Ca_2Na\}[Mn_2^{2+}](V_3^{5+})O_{12}$ and schäferite, $\{Ca_2Na\}[Mg_2](V_3^{5+})O_{12}$, which have the cubic garnet structure, vanadium in most natural silicate garnets is considered to be present as V^{3+}, as in the mineral species goldmanite, $\{Ca_3\}[V_2](Si_3)O_{12}$, and even when the element is present in only minor or trace quantities (Locock et al., 1995). Similarly, manganese generally occurs as Mn^{2+}, with the exception of highly oxidized compositions in which Mn^{3+} is present, e.g., the garnet-related tetragonal mineral henritermierite, $\{Ca_3\}[Mn_2^{3+}](SiO_4)_2(OH)_4$ (Armbruster et al., 2001). The relative concentrations of Fe^{3+} and Fe^{2+} in garnet can be determined by several methods including classical titrimetry, colorimetry, ^{57}Fe Mössbauer spectroscopy, synchrotron-based X-ray absorption spectroscopy or by calculation from stoichiometric constraints. The topic of the valence state of Ti in garnet is more contentious and is addressed below.

2.3. The valence state of Ti

The major redox couple in natural garnet is the Fe^{3+}–Fe^{2+} pair. Yet, for some natural Ti-rich garnets, the presence of both Ti^{4+} and Ti^{3+} has occasionally been invoked, generally to satisfy the requirement of exact charge balance (and usually without consideration of the effects of propagated analytical uncertainty). The crystal chemistry of Ti-bearing garnets has been carefully evaluated in recent years (Armbruster et al., 1998; Chakhmouradian and McCammon, 2005; Locock et al., 1995), and the existence of Ti^{3+} in natural garnets is not supported by these investigations.

From the perspective of both standard reduction potentials and of geologically relevant oxygen fugacity buffers (cf. Frost, 1991), the reducing conditions required for Ti^{3+}-in-garnet are not likely to occur in terrestrial garnet-forming environments: e.g., the Ti_3O_5–TiO_2 oxygen fugacity buffer is ~4–5 log units below the iron–wüstite buffer at ~1400 K (Ihinger and Stolper, 1986). Although measurement of the intrinsic oxygen fugacities of natural Ti-bearing garnets yielded results close to the iron–wüstite buffer and the iron–quartz–fayalite buffer (Virgo et al., 1976); such types of measurements have been