

## Appendix 4. Description of the Excel spreadsheet

### Purpose

Appendix 4 is intended to determine the dominant species present from a chemical analysis of a natural garnet. This appendix consists of an Excel spreadsheet that can accept up to 50 analyses at a time, and yields for each analysis its group and species, as well as an empirical formula.

### Input

The data from a chemical analysis are entered into the Data\_Report worksheet as oxides in percent by weight, with the exception of fluorine, which is entered as the element in percent by weight. Mathematical operations are undertaken on the linked Calculation worksheet; data should not be input directly into this latter worksheet. The list of inputs for the Data\_Report worksheet in percent by weight includes: SiO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, SnO<sub>2</sub>, HfO<sub>2</sub>, ThO<sub>2</sub>, UO<sub>3</sub>, TeO<sub>3</sub>, Sb<sub>2</sub>O<sub>5</sub>, As<sub>2</sub>O<sub>5</sub>, V<sub>2</sub>O<sub>5</sub>, Nb<sub>2</sub>O<sub>5</sub>, P<sub>2</sub>O<sub>5</sub>, Y<sub>2</sub>O<sub>3</sub> (include REE<sub>2</sub>O<sub>3</sub> as the equivalent proportion of Y<sub>2</sub>O<sub>3</sub> along with the measured Y<sub>2</sub>O<sub>3</sub> content), Al<sub>2</sub>O<sub>3</sub>, Sc<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>3</sub>, FeO, Fe<sub>2</sub>O<sub>3</sub> (but see below), ZnO, MnO, MgO, CaO, Na<sub>2</sub>O, Li<sub>2</sub>O, H<sub>2</sub>O<sup>+</sup> (water of crystallization), and F. Any correction needed for the oxygen equivalence of fluorine is calculated by the spreadsheet. The user must decide whether any vanadium content is expressed as V<sub>2</sub>O<sub>3</sub> or V<sub>2</sub>O<sub>5</sub>.

If the total iron content of the analysis is entered as FeO (wt.%), then the method of Droop (1987) is used to calculate the proportions of Fe<sup>2+</sup> and Fe<sup>3+</sup> and Mn<sup>2+</sup> and Mn<sup>3+</sup> (this latter constituent only in the absence of Fe<sup>2+</sup>) on the basis of 12 anions, where the anions are the sum of O<sup>2-</sup>, (OH)<sup>-</sup>, and F<sup>-</sup>. If the user inputs some or all of the iron content as Fe<sub>2</sub>O<sub>3</sub> (wt.%), then this calculation of Fe<sup>2+</sup> and Fe<sup>3+</sup>, and Mn<sup>2+</sup> and Mn<sup>3+</sup>, is not performed. In any case, the user should not input Mn<sub>2</sub>O<sub>3</sub>, but rather allow the spreadsheet to calculate this quantity as necessary.

The cation proportions are calculated on the basis of 12 anions, with charge-balance used (as described above) to attempt to obtain a total of 8 non-H cations. The elements or valences B, S, K, V<sup>2+</sup>, Ni, Ga, Ge, Sr, Ba, Pb, and U<sup>4+</sup> are not included in the spreadsheet.

For analyses suspected to be of the tetragonal-symmetry minerals henritermierite or holtstamite, the entry FALSE should be given in the cells that query “cubic? (true / false)”, whereas for other hydrous garnets, TRUE should be entered. For convenience, the lower symmetry and distinct structures of the tetragonal garnets are otherwise ignored in this spreadsheet.

### Site allocation of cations

Appendix 4 allocates the cations to the three distinct structural sites using an inflexible set of assumptions. It need hardly be stated that structural and/or spectroscopic data are preferable to using such an algorithm, but such information is not commonly available for large data sets, in contrast to the abundant chemical data obtained from electron microprobe analyses.

The site allocation assumptions follow those of Table 3 of the manuscript. The priority of filling each cation site is summarized here as follows:

$$Z > Y > X;$$

$$Z = (\text{As}, \text{V}^{5+}, \text{P}, \text{Li}, \text{Zn}) > \text{Si} > \text{Al} > \text{Fe}^{3+} > \text{Fe}^{2+}, \text{Ti};$$

$$Y = (\text{Zr}, \text{Sn}, \text{Hf}, \text{U}, \text{Te}, \text{Sb}, \text{Nb}, \text{Sc}, \text{Cr}, \text{V}^{3+}) > (\text{Si}, \text{Ti}, \text{Al}, \text{Mn}^{3+}, \text{Fe}^{3+}) > \text{Mg} > \text{Fe}^{2+} > \text{Mn};$$

$$X = (\text{Y}, \text{Ca}, \text{Na}, \text{Mn}, \text{Fe}^{2+}, \text{Th}) > \text{Mg}.$$

As per the manuscript, hydrogen is incorporated via the “hydrogarnet substitution”:  $4\text{H} + {}^Z\Box \rightarrow \Box + {}^Z\text{Si}$ , and tetrahedral vacancies are also assumed if fluorine is present in the absence of corresponding quantities of lithium.

#### Extended dominant-constituent rule

Hatert and Burke (2008) defined “the *rule of the dominant constituent*: a mineral is a distinct species if the set of dominant constituents at the sites in the crystal structure is distinct from that of any other mineral with the same structural arrangement.” Because of “cases of coupled heterovalent–homovalent substitutions”, it was necessary for the rule to be “extended with the dominant-valency rule by considering a group of atoms with the same valency state as a single constituent.” And therefore, “the extension [of the dominant-constituent rule] with the dominant-valency rule is necessary to establish charge-balanced end-member formulae for solid-solution series with complex mechanisms of substitution” (Hatert and Burke 2008).

In the garnet supergroup, in which the approved species (manuscript Table 1) are formulated as end-members, following Hawthorne (2002), the effect of the *extended dominant-constituent rule* is to arrange the end-members into general charge-balanced formulae. This is reflected in the classification of the approved species, in which the end-members are classified into groups by the effective charge of the Z site.

The spreadsheet determines group and species in accord with the extended dominant-constituent rule. For each cation site, the spreadsheet sums the homovalent cations that occupy that site. For example, for the X site,  $\text{Ca} + \text{Mg} + \text{Mn} + \text{Fe}$  yields the sum of the divalent ions, the sodium content gives the value for monovalent ions, and yttrium yields the value for trivalent ions. From the proportions of the dominant valences, the maximum content of each type of charge-balanced end-member formula is then calculated. These maxima are calculated separately from each other. However, in several cases, the proportions of different end-member formulae may be limited by the same minimum quantity of a valence state, e.g.,  $\text{Na}^+$ , present in the analysis. In such cases, the maximum contents of the end-member formulae are not independent, and their sum will therefore exceed 100%.

72 Having found the most abundant charge-balanced formula, the group to which it belongs is  
73 assigned (manuscript Table 1). From the assignment of the group, and from the site allocations of  
74 the cations, the principal cations that occupy the charge-balanced formula of that group are  
75 determined, and thus the dominant species is assigned. A set of hypothetical end-members is  
76 included in the calculations of the spreadsheet to assist in the rare cases in which an approved  
77 species is not found for an analysis.

## 79 Results and empirical formula

80 From the allocation of the cations, and the anions determined from the chemical analysis, a  
81 preliminary empirical formula is given, with the quantities rounded to a maximum of three decimal  
82 places. The constituents of the empirical formula are ordered by atomic site, and organized in each  
83 site by decreasing abundance. The results, including group, dominant species, and empirical  
84 formula, are given below each corresponding original analysis on the Data\_Report worksheet.

85 Because of the limitations of text formats for calculated cells in Excel, the cations  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$   
86 are given respectively as Feii and FeIII in the *Y* and/or *Z* sites of an empirical formula. Similarly,  
87  $\text{Mn}^{2+}$  and  $\text{Mn}^{3+}$  are reported on the *Y* site of an empirical formula as Mnii and MnIII. In contrast,  
88 cations whose occurrence is restricted to a given site, e.g.,  $\text{V}^{3+}$  on the *Y* site, are expressed without  
89 any charge designation, as there should be no ambiguity as to their identities. Cation vacancies on  
90 the *Z* site are not shown explicitly in the formulae yielded by the Excel spreadsheet, but are  
91 established by difference from the ideal proportions, and from the presence of F and/or OH.