21	The systematics of the spinel-type minerals: an overview
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ABSTRACT

30 Compounds with a spinel-type structure include mineral species with the general formula $AB_2\varphi_4$, where φ can be O^{2-} , S^{2-} , or Se^{2-} . Space group symmetry is $Fd\overline{3}m$, even if lower symmetries 31 are reported owing to the off-centre displacement of metal ions. In oxide spinels ($\varphi = O^{2-}$), A and B 32 cations can be divalent and trivalent ("2-3 spinels") or, more rarely, tetravalent and divalent ("4-2 33 spinels"). From a chemical point of view, oxide spinels belong to the chemical classes of oxides, 34 germanates, and silicates. Up to now, 24 mineral species have been approved: ahrensite, 35 brunogeierite, chromite, cochromite, coulsonite, cuprospinel, filipstadite, franklinite, gahnite, 36 galaxite, hercynite, jacobsite, magnesiochromite, magnesiocoulsonite, magnesioferrite, magnetite, 37 manganochromite, qandilite, ringwoodite, spinel, trevorite, ülvospinel, vuorelainenite, and 38 zincochromite. Sulfospinels ($\phi = S^{2-}$) and selenospinels ($\phi = Se^{2-}$) are isostructural with oxide 39 spinels. Twenty-one different mineral species have been approved so far; of them, three are 40 selenospinels (bornhardtite, trüstedtite, and tvrrellite), whereas 18 are sulfospinels: cadmoindite, 41 42 carrollite, cuproiridsite, cuprokalininite, cuprorhodsite, daubréelite, ferrorhodsite, fletcherite, florensovite, greigite, indite, kalininite, linnaeite, malanite, polydymite, siegenite, violarite, and 43 xingzhongite. The known mineral species with spinel-type structure are briefly reviewed, indicating 44 for each of them the type locality, the origin of the name, and a few more miscellaneous data. This 45 review aims at giving the state-of-the-art about the currently valid mineral species, considering the 46 47 outstanding importance that these compounds cover in a wide range of scientific disciplines.

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49 *Keywords*: spinel, oxide spinel, sulfospinel, selenospinel.

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51

Introduction

52 Compounds with spinel-type structure occupy an outstanding position not only in Geology, 53 but also in many branches of science and their crystal structure represent one of the archetype structures based on a cubic close packing of anions. Owing to its quite simple structure-type, spinel 54 55 was one of the very first minerals whose structure has been determined after the discovery of the X-56 ray diffraction by crystals (Nishikawa 1914; Bragg 1915). Indeed, in the ideal structure topology of spinel, the only variables to be refined are the unit-cell parameter a, a single positional parameter 57 for the anion, the displacement parameters for the three independent sites, and the cation site 58 occupancies. Despite this apparent simplicity, several detailed crystal-chemical studies were carried 59 out on spinels (and on their synthetic analogues), pointing out some interesting crystal-chemical 60 61 features related to cation disordering with important consequences on their thermo-chemical and physical properties. As an example, the mechanism of incorporation of the cations within the 62 structures, their partitioning as a function of temperature and pressure conditions, the thermal 63 expansion and the compressibility of the spinel structure may be of interest for the modelization of 64 the Earth's mantle. In fact, a silicate phase with spinel structure represents the result of the 65 66 transformation of olivine under high pressure conditions typical of the transition zone, between 410 and 660 km deep, and this high-pressure polymorph (γ -Mg₂SiO₄, also known as the mineral 67 ringwoodite) is considered one of the major phases in the Earth's mantle (e.g., Frost 2008). Besides 68 their enormous petrological importance, spinels are used as geothermometers, geobarometers, and 69 70 geospeedometers, and they can represent important guides to the mining exploration (e.g., Heimann et al. 2005). Some spinels are ore minerals (e.g., magnetite for iron; violarite for nickel) and others 71 72 can be used as gemstones. The well-known "balas Ruby" is actually a red-coloured variety of spinel, used since long time; some of the most famous gemstones are indeed spinels, e.g. the Black 73 Prince's Ruby and the Timur ruby in the British Crown Jewels. Spinels are actively studied by solid 74 75 state scientists, for their electric and magnetic properties: it is noteworthy that one of the most 76 common spinels, magnetite, is likely to be related with the discovery of magnetism, as reported by 77 the Roman naturalist Pliny the Elder (23-79 AD). Finally, spinels could form attractive mineral specimens, with octahedral, cube-octahedral, and cubic crystals, sought by mineral collectors and 78 79 mineralogical museums (Fig. 1).

Mineral phases having a spinel-type structure belong to the chemical groups of oxides and sulfides, and more rarely to selenides, silicates, and germanates. In this paper we present selected basic data on the 24 known oxide spinels and, for sake of completeness, we report the same data for the 21 known natural sulfospinels and selenospinels, namely sulfides and selenides having a spineltype structure. For each entry, basic information is given: the type locality, the origin of the name, and a few more miscellaneous data. Moreover, mention is made of recent structural refinements,

86 possibly carried out on natural compounds or, in the lack of it, on its synthetic analogue.

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Crystal structure of spinels

The spinel structure (Fig. 2) is based on a cubic close packing of anions, with cations hosted within tetrahedral (T) and octahedral (M) sites (e.g., Hill et al. 1979). The space group symmetry is $Fd\bar{3}m$, even if some phases show a lowering of symmetry due to the off-center displacement of metal ions along the [111] direction (e.g., Higgins et al. 1975). Cations in tetrahedral and octahedral coordination occupy the 8*a* (point symmetry $\bar{4}3m$) and 16*d* (point symmetry . $\bar{3}m$) positions, respectively. Anions are hosted at the 32*e* positions (point symmetry .3*m*), which require, for their complete description, an additional parameter, usually indicated as oxygen parameter.

The general formula of spinel-type minerals can be written as $AB_2\varphi_4$. For oxide spinels (having $\varphi = O^{2-}$), the formal charges of *A* and *B* cations can be +2 and +3 in the so-called "2–3 spinels" and +4 and +2 in the so-called "4–2 spinels". Considering the sulfo- and selenospinels, having $\varphi = S^{2-}$ or Se²⁻, there are some uncertainties in the assessment of the actual ion oxidation states, as stressed by Vaughan and Craig (1978). For example, three electronic structure models have been proposed for the synthetic spinel CuCr₂Se₄: Cu²⁺Cr³⁺₂Se²⁻₄ (Goodenough 1967), Cu⁺(Cr³⁺Cr⁴⁺)Se²⁻₄ (Lotgering 1964) and Cu⁺Cr³⁺₂(Se²⁻₃Se⁻) (Lotgering and Van Stapele 1967).

103 The real spinel-type structures can display variable degrees of disorder of the *A* and *B* 104 cations over the T and M sites. This disorder can be described using the inversion parameter *i*, 105 which is defined as the fraction of the *B* cations at the T sites. The inversion parameter *i* can vary 106 from 0, in the completely normal spinel, ${}^{T}A^{M}B_{2}\varphi_{4}$, to 1, in the completely inverse spinels, 107 ${}^{T}B^{M}(AB)\varphi_{4}$. A totally disordered configuration is obtained for *i* = 0.67.

108

Oxide spinels

Oxide spinels include 24 different mineral species (Table 1), that can be classified as "2-3 spinels" $(A^{2+}B^{3+}_{2}O_{4})$ and "4-2 spinels" $(A^{4+}B^{2+}_{2}O_{4})$. Considering the "2-3 spinels", the various mineral species can be grouped as a function of the dominant B^{3+} cation, forming four different groups, characterized by Al, Cr, Fe, and V as *B* cation. "4-2 spinels", rarer than the former group, has Fe²⁺, Mg²⁺, and Mn²⁺ as *B* cation, whereas the *A* cation is represented by a tetravalent cation (Si, Ti, and Ge) or by a combination of pentavalent and trivalent cations, like in filipstadite. In the following we describe the oxide spinels sorted alphabetically.

- 116
- 117 **Ahrensite** SiFe₂O₄

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Ahrensite is a silicate spinel, the Fe^{2+} analogue of ringwoodite and the most recent entry among minerals with the spinel structure. It has been found in the Tissint Martian meteorite recovered in Morocco in October 2011 (Ma et al. 2013). The name honours Thomas J. Ahrens, geophysicist at the California Institute of Technology. Crystal structure of synthetic SiFe₂O₄ spinel was refined by several authors (e.g., Yagi et al. 1974; Yamanaka et al. 2001).

123

124 Brunogeierite - GeFe₂O₄

Brunogeierite was first described from Tsumeb, Namibia (Ottemann and Nuber 1972). 125 There were some uncertainties about the oxidation state of germanium and iron in this mineral. In 126 the type description, electron-microprobe data were presented with all germanium given as GeO₂; 127 however, after Fleischer and Mandarino (1995), the mineral was assumed to have ideal formula 128 Ge²⁺Fe³⁺₂O₄, and this formula was reported in most mineralogical treatises and compilations, even 129 if the +2 oxidation state of germanium is unlikely in natural phases. Cempírek and Groat (2013), on 130 131 the basis of bond-valence calculations carried out using a structural model of brunogeierite obtained with single-crystal X-ray diffraction data (Welch et al. 2001), redefined the correct chemical 132 formula as Ge4+Fe2+2O4. Brunogeierite has been named after dr. Bruno H. Geier (1902-1987), 133 formerly chief mineralogist of the Tsumeb Corporation. Brunogeierite is a germanate spinel. 134

135

136 Chromite $- FeCr_2O_4$

The name chromite was introduced in the mineralogical literature by Haidinger (1845) in 137 138 allusion to its composition. The type locality is considered Gassin, Var, France (Gallitzin 1801). Today the term chromite refers to the Fe endmember along the join $MgCr_2O_4 - FeCr_2O_4$; synthetic 139 binary join was studied through single-crystal X-ray diffraction by Lenaz et al. (2004) and through 140 Raman spectroscopy by Lenaz and Lughi (2013). Due to the extensive solid solution between the 141 two endmembers, it is likely that several alleged occurrences of chromite actually consist of 142 143 magnesiochromite, the Mg endmember. Moreover, chromite forms solid solutions with other oxide spinels, like hercynite, spinel, magnetite, coulsonite, zincochromite, cochromite, and 144 manganochromite. Recent structural refinements of natural chromites from the Bushveld Complex, 145 South Africa, are reported by Lenaz et al. (2007). 146

147

148 **Cochromite** $- CoCr_2O_4$

Cochromite was first described from the Bon Accord nickel deposit, Barberton, South Africa (De Waal 1978), in a trevorite-liebenbergerite-bunsenite metamorphic assemblage, as a relict phase rimmed by trevorite. This is the only known occurrence. The name is after its chemical

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composition. At the type locality, Co^{2+} is partially replaced by Fe^{2+} and Ni^{2+} . Some samples have Ni 152 > Co, and potentially represent a distinct mineral species, NiCr₂O₄. Indeed, De Waal (1978) called 153 154 that phase "nichromite", but it was never submitted to the IMA CNMNC for approval; therefore "nichromite" is not considered a valid mineral species (and for this reason it is omitted from the 155 156 present compilation). More recently, another Co-rich spinel was described from Bo Ploi, Thailand 157 (Guo et al. 1994). Its endmember composition is $CoAl_2O_4$ and this could represent another distinct species. Crystal structure data on cochromite are not available but Garcia Casado and Rasines 158 (1986) refined the structure of synthetic $CoCr_2O_4$. Structural data on synthetic $CoAl_2O_4$ are known 159 as well (Ardit et al. 2012). 160

161

162 **Coulsonite** $- FeV_2O_4$

The original description of coulsonite was made on a sample from Bihar, India (Dunn 1937) 163 as patches in magnetite, intergrown with ilmenite and replaced by hematite. The name honours dr. 164 Arthur Lennox Coulson (1898-?), geologist of the Indian Geological Survey. Owing to the poor 165 characterization of this mineral, it was also hypothesized that coulsonite from Bihar could be 166 167 nothing but vanadium-bearing maghemite (Frankel and Grainger 1941). Then, coulsonite was redefined and properly characterized after a new occurrence at the Buena Vista Hills, Lovelock, 168 Nevada, USA (Radtke 1962). Crystal structure data on coulsonite are not available, whereas Reuter 169 et al. (1969) refined the crystal structure of synthetic FeV₂O₄. 170

171

Cuprospinel - CuFe₂O₄

173 Cuprospinel was first described by Nickel (1973) from the heavily oxidized dump of the 174 Consolidated Rumbler mines Limited, near Baia Verte, Newfoundland, Canada, in close association 175 with hematite; this is the only known occurrence. Name is after its chemical composition. The 176 investigation showed that the dump was originally formed by Cu-Zn ore that had ignited 177 spontaneously and smouldered at intervals. Consequently, cuprospinel formed under particular 178 environmental conditions. Crystal structure data on cuprospinel are not available but the crystal 179 structure of synthetic CuFe₂O₄ was refined by Mexmain (1971).

180

181 Filipstadite – $(Sb_{0.5}Fe_{0.5})Mn_2O_4$

The mineral was first described from Långban, Värmland, Sweden (Dunn et al. 1988) and named after the city of Filipstad, near which the Långban mine is located. The ideal chemical formula is $(Sb^{5+}_{0.5}Fe^{3+}_{0.5})(Mn^{2+},Mg)_2O_4$. The oxidation state of manganese, antimony, and iron is assumed on crystal-chemical and stoichiometric grounds. Sb^{5+} and Fe^{3+} must share the same site and this is a case of valency-imposed double site-occupancy (Hatert and Burke 2008). A recent and accurate structural study of filipstadite was carried out in a cubic supercell with a cell edge three times longer than the normal one (Bonazzi et al. 2013). The comparison of new electronmicroprobe data and single-crystal X-ray diffraction data led Bonazzi et al. (2013) to propose a quite complex distribution of cations over six M and five T sites in the supercell.

191

192 Franklinite $- ZnMn_2O_4$

The mineral was first described by Berthier (1819) and named after its type locality, the Franklin mine, New Jersey, USA. Both the mine and the mineral took their name in honour of the scientist and statesman Benjamin Franklin (1706-1790), one of the founding fathers of the United States of America. At the type locality, franklinite contains minor Mn^{2+} substituting for Zn^{2+} . Crystal structure refinements of $ZnMn_2O_4$ spinel, both natural or synthetic, have been reported by several authors (e.g., Lucchesi et al. 1997, 1999; Pavese et al. 2000), indicating a normal cation distribution.

200

201 **Gahnite** $- ZnAl_2O_4$

First described by von Moll (1807) from the Falun copper mine, Dalama, Sweden, gahnite was named after the Swedish chemist and mineralogist Johan Gottlieb Gahn (1745-1818). The crystal structure of gahnite from the type locality was solved by Saalfeld (1964) and several structural refinements are known, both on natural (e.g., D'Ippolito et al. 2013) and synthetic ZnAl₂O₄ (Rietveld method on powder: Popović et al. 2009; single crystal: Ardit et al. 2012).

207

Galaxite - MnAl₂O₄

This mineral was first described by Ross and Kerr (1932) from a vein containing unusual 209 Mn minerals equilibrated under amphibolites facies conditions near Bald Knob, North Carolina, 210 USA. It was named galaxite to distinguish it from the synthetic analogue, manganspinel, described 211 by Krenner in 1907 from an iron-furnace slag (Spencer 1922, and references therein). The name 212 recalls galax, that grows abundantly in North Carolina, and the city of Galax, Virginia, where Mr. 213 214 Crabill lived. He had long been interested in the geology and mineralogy of the type locality of galaxite, and he had often given his assistance to visiting geologists. Galaxite is a normal spinel, 215 whose crystal structure was reported by Essene and Peacor (1983) and Lucchesi et al. (1997). 216 217 Structural and spectroscopic data on synthetic $MnAl_2O_4$ are known as well (Hålenius et al. 2007).

218

219 **Hercynite** - FeAl₂O₄

The mineral was discovered by Zippe (1839) and named after the type locality (Poběžovice, Bohemian Forest – in Latin *Silva Hercynia* – Czech Republic). Several single-crystal and powder structures of natural hercynite are available in literature (e.g., Larsson et al. 1994; Harrison et al. 1998); the series $FeAl_2O_4$ – $FeCr_2O_4$ was studied by single-crystal X-ray diffraction and FTIR (Lenaz and Skogby 2013). Recently, Lavina et al. (2009) discussed the intracrystalline cation distribution on two sets of fast-cooled anatectic and slow-cooled metamorphic hercynites.

226

Jacobsite - MnFe₂O₄

The mineral was first found at the Jakobsberg mine, Värmland, Sweden (Damour 1869) and 228 named *jakobsite* after the type locality. The name was then changed in jacobsite (e.g., Johannson 229 1928). Whereas, according to Essene and Peacor (1983), wide solvi at metamorphic temperatures 230 separate spinel ferrites (jacobsite, franklinite, magnesioferrite, and magnetite) from spinel 231 aluminate, Beard and Tracy (2002) observed an extensive miscibility along the galaxite-jacobsite 232 join. The crystal chemical role of Mn in spinels has been widely investigated owing to the tendency 233 of Mn to exist in two main oxidation states, i.e. Mn^{2+} and Mn^{3+} . In jacobsite, this difficulty is 234 enhanced by the equilibrium $Mn^{2+} + Fe^{3+} = Mn^{3+} + Fe^{2+}$ and the occurrence of electron hopping 235 between adjacent sites, making the correct assignment of oxidation states difficult. Single-crystal 236 structure refinements of jacobsite from the type locality confirmed the normal character of 237 iacobsite, with Mn^{2+} preferentially hosted at the tetrahedral site (Lucchesi et al. 1997). 238

239

240 Magnesiochromite – $MgCr_2O_4$

Magnesiochromite is the magnesium analogue of chromite. In early literature, this mineral was given the name *magnochromite* (Bock 1868; Websky 1873) and the currently accepted name was first introduced by Lacroix (1910). Even later, Fisher (1929) suggested an unlikely distinction between *magnochromite* (the pure Mg endmember) and magnesiochromite (intermediate member along the join MgCr₂O₄ – FeCr₂O₄), which is today obsolete. The type locality is Schwarzenberg, Saxony, Germany. Several single-crystal structure refinements of magnesiochromite are available, sometimes hidden under the name "chromite" (e.g., Lenaz et al. 2009).

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$249 \qquad \textbf{Magnesiocoulsonite} - MgV_2O_4$

This mineral was first described from the Pereval marble quarry, southern Baikal region, Russia (Reznitsky et al. 1995) and was named for its relationship with coulsonite, being its magnesium analogue. No other occurrences are known so far. The crystal structure of synthetic MgV_2O_4 was refined by Reuter et al. (1983).

$255 \qquad \textbf{Magnesioferrite} - MgFe_2O_4$

First discovered at Fosso del Cancherone and in the fumaroles of 1855 eruption of the Monte Somma–Vesuvius volcanic complex, Italy, and described by Rammelsberg (1859) under the name *magnoferrite*. Its current name was later attributed by Dana (1892). Several studies on the cation ordering in magnesioferrite at high temperature and high pressure conditions were carried out on synthetic compounds (O'Neill et al. 1992; Antao et al. 2005a, 2005b). The synthetic series $MgCr_2O_4 - MgFe_2O_4$ was studied by Lenaz et al. (2006) and Lenaz and Lughi (2013).

262

263 **Magnetite** $- FeFe_2O_4$

Magnetite is a very common mineral, used since long time for iron metallurgy, and known under different names (e.g., lodestone); Haidinger (1845) mentioned it with its current name magnetite. The type locality is unknown. It is noteworthy that the very first analytical determination of the crystal structure of a member of the spinel group was carried out using a crystal of magnetite (Nishikawa 1914; Bragg 1915). Since then, several structural studies were carried on (e.g., Fleet 1984; Della Giusta et al. 1987).

270

271 Manganochromite – MnCr₂O₄

Manganochromite is a very rare mineral species first described from the metamorphosed 272 pyrite deposit of Shepherd Hill (Brukunga quarry), Nairne, Mt Lofty Ranges, South Australia, 273 Australia, by Graham (1978). It occurs as euhedral grains up to 80 μ m \times 800 μ m at the contact 274 275 between pyrrhotite and gangue minerals. The name manganochromite was given by analogy with the name magnesiochromite, of which manganochromite is the Mn-analogue. At the type locality, 276 Cr is partially replaced by V, showing extensive solid solution with vuorelainenite, as observed by 277 Zakrzewski et al. (1982) at the Sätra mine, Sweden. Crystal structure data on manganochromite are 278 not available; the structure of synthetic $MnCr_2O_4$ was refined by Raccah et al. (1966). 279

280

281 **Qandilite** $- TiMg_2O_4$

Qandilite is a very rare "4-2 spinel", first described from a forsterite skarn in contact with a banded diorite, in the Dupezeh Mountain, Qala-Dizeh region, Iraq (Al-Hermezi 1985). The mineral has been named after the metamorphic Qandil group in which it occurs. With respect to the ideal endmember formula TiMg₂O₄, some Fe³⁺ partially substitutes for Mg²⁺ and Ti⁴⁺, and the formula should be better written (Ti,Fe³⁺)(Mg,Fe³⁺)₂O₄. Before the type description, qandilite was found in the Kangerdlugssuaq region, East Greenland, by Gittins et al. (1982); qandilite from Greenland is closer to the endmember composition than that from the type locality, containing 86 mol% TiMg₂O₄. Crystal structure data are available only on the synthetic counterpart, TiMg₂O₄ (e.g., Wechsler and Von Dreele 1989; Bosi et al. 2014).

291

292 **Ringwoodite** - SiMg₂O₄

293 Ringwoodite is a silicate spinel and it is the high-pressure isometric polymorph of forsterite 294 and wadsleyite. It was first reported by Binns et al. (1969) from the Tenham meteorite, a chondritic meteorite found in Australia. Ringwoodite occurs as rounded grains up to 100 µm in veinlets cutting 295 the matrix and as pseudomorph after olivine; its origin is probably related to the shock 296 metamorphism. Ringwoodite has been named in honour of Alfred Edward Ringwood (1930-1993), 297 geochemist of the Australian National University, Canberra, Australia. Since the first description, 298 ringwoodite has been reported from several meteorites; the only description of ringwoodite in Earth 299 material was given by Xie et al. (1986) from spinel-lherzolite xenoliths found in the Hannuoba 300 basalt field, Hebei Province, China. Owing to the important petrological role played by ringwoodite 301 in the Earth's transition zone, several crystal structure studies have been performed using synthetic 302 303 Si(Mg,Fe)₂O₄ (e.g., Hazen et al. 1993; Smyth et al. 2003; Ye et al. 2012).

304

$305 \quad Spinel - MgAl_2O_4$

It is the eponymous mineral, known since the antiquity and rewarded for its gemological properties. The first traces of the name date back to the early 17th Century (e.g., de Boodt et al. 1647). The name spinel is likely to come from the Latin *spina* (thorn), in allusion to the pointed shape of the crystals. The name today refers to one of the most common among oxide spinels, the Mg-Al endmember. There is a lot of experimental work on the structural behavior of spinel at different T and P conditions, carried out mainly on synthetic products; it is noteworthy that the *American Mineralogist Crystal Structure Database* lists 600 records under the label "spinel".

313

314 **Trevorite** - NiFe₂O₄

Trevorite is a relatively rare Ni-Fe spinel, first incompletely described by Crosse (1921) from the Bon Accord nickel deposit, South Africa. Then, Walker (1923) gave a full description of this spinel, whose name honours Tudor Gruffydd Trevor (1865-1958), geologist and mining prospector in the Pretoria District. Further data were given by Partridge (1944) and De Waal (1969, 1972). The latter author, studying the nickel minerals from the Bon Accord deposits, described the existence of intermediate members between trevorite and magnetite and gave new data about the former. The crystal structure of synthetic NiFe₂O₄ was refined by Blesa et al. (1993).

323 Ulvöspinel – TiFe₂O₄

The mineral was first reported from the Södra Ulvön, Ångermanland, Sweden by Mogensen (1946) and named after its type locality and its belonging to the oxide spinels. Ramdohr (1953) evidenced that ulvöspinel is a common constituent of titaniferous magnetite, as very thin exsolution lamellae. Crystal structure refinements are available for both natural and synthetic compound (e.g., Stout and Bayliss 1980; Bosi et al. 2009). Ulvöspinel is a "4-2 spinel".

329

$330 \quad Vuorelainenite - MnV_2O_4$

First described from the Sätra pyrite mine, Östergötland, Sweden (Zakrzewski et al. 1982), 331 vuorelainenite is a rare Mn-V spinel showing a wide solid solution with manganochromite, as 332 shown by the considerable amount of Cr^{3+} substituting for V^{3+} at the type locality. Several years 333 before the type description, analyses of an oxide spinel corresponding to vuorelainenite, and closer 334 to the endmember composition, were reported from Outokumpu, Finland (Long et al. 1963). The 335 mineral has been named after Yrjö Vuorelainen (b. 1922), exploration geologist with the 336 Outokumpu Company and discoverer of the Outokumpu manganese-vanadium spinel. Crystal 337 structure data on the natural compound are not available, whereas Plumier (1962) refined the 338 339 structure of synthetic MnV₂O₄.

340

341 **Zincochromite** $- ZnCr_2O_4$

Zincochromite is a rare member of the spinel group first found at the Srednyaya Padma uranium-vanadium mine, close to Lake Onega, Karelia Republic, Russia (Nesterov and Rumyantseva 1987), where it occurs as very small euhedral crystals (rarely up to 50 μ m), resulting from the breakdown of chromian aegirine. It was named after its composition and the relationship with chromite. Crystal structure data on zincochromite are not available, whereas the structure of synthetic ZnCr₂O₄ was refined by several authors (e.g., O'Neill and Dollase 1994; Levy et al. 2005).

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Sulfospinels and selenospinels

Sulfospinels and selenospinels are isostructural with oxide spinels, with the anion represented by sulfur and selenium, respectively. As pointed out by Vaughan and Craig (1978), a very large number of synthetic spinel structure compounds with sulfur, selenium, and also tellurium, have been reported. Actually, 21 natural occurring sulfo- and selenospinels are known to occur (Table 2). Among them, bornhardtite and xingzhongite seem to be questionable. Mineral
 species are described below in alphabetical order.

357

358 **Bornhardtite** – CoCo₂Se₄

359 Bornhardtite was described by Ramdohr and Schmitt (1955) from the Trogtal quarry, Harz, 360 Lower Saxony, Germany, as inclusions in clausthalite, together with three other cobalt selenides: trogtalite, hastite, and an unnamed mineral, later named freboldite. Bornhardtite has been named in 361 honour of Wilhelm Bornhardt (1864-1946), German student of ore deposits. The identifications of 362 these cobalt selenides were based exclusively on X-ray powder diffraction data collected on drilled-363 out material containing a mixture of selenides; in addition, the identifications relied on the 364 365 paragenesis, hardness, and optical properties. Chemical analyses were not performed and the assumption that the mineral are cobalt selenides were made indirectly, owing to i) the occurrence of 366 cobalt in the selenide ore from Trogtal, ii) the similarity between the diffraction pattern to 367 sulfospinels, and iii) to the distinct violet to reddish brown color in reflected light microscopy 368 typical of cobalt minerals. Recently, Keutsch et al. (2009) re-examined one of these phases, hastite, 369 370 the orthorhombic polymorph of CoSe₂, which was discredited since it corresponded to ferroselite, FeSe₂. Consequently, bornhardtite could be considered questionable and further studies are required 371 372 to confirm its status as a valid mineral species.

373

374 **Cadmoindite** $- CdIn_2S_4$

This mineral was found as octahedral crystals up to 0.15 mm in the high-temperature fumaroles (T = 450-600°C) of Kudriavy volcano, Kurily, Russia (Chaplygin et al. 2004). X-ray diffraction showed that cadmoindite is the analogue of synthetic CdIn₂S₄. Crystal structure analysis on natural specimen has not been carried out, whereas Hahn and Klinger (1950) solved the crystal structure of synthetic CdIn₂S₄. Cadmoindite is the cadmium analogue of indite and the name is after its chemical composition.

381

382 **Carrollite** $- CuCo_2S_4$

Carrollite was first described by Faber (1852) as a copper-cobalt sulfide with composition Cu₂Co₂S₄ on specimens from Finksburg, Carroll County, Maryland, USA. It has been named from the type locality. The status of carrollite as a distinct mineral species from linnaeite was questioned (e.g., Shannon 1926). Meanwhile, Laspeyres (1891) assigned the name "sychnodymite" to a copper-cobalt sulfide from Siegen, Germany. De Jong and Hoog (1928) demonstrated through Xray data the identity of carrollite and "sychnodymite". Tarr (1935) examining chemical data from literature confirmed the validity of carrollite as mineral species, discrediting "sychnodymite", considered as a Ni-rich variety of carrollite. However, according to Wagner and Cook (1999), no evidence for wide solid solution between carrollite and fletcherite, $CuNi_2S_4$, is known. Charnock et al. (1990) pointed out the tetrahedral coordination of Cu through extended X-ray absorption fine structure (EXAFS) spectroscopy, whereas X-ray absorption spectroscopy (XAS) demonstrated that the valence state of this element in carrollite is Cu^+ (Pattrick et al. 2008) and not Cu^{2+} as previously reported (e.g., Charnock et al. 1990).

396

397 **Cuproiridsite** - CuIr₂S₄

Cuproiridsite was first described by Rudashevsky et al. (1985) from alluvial deposits found
in the Aldan shield and in Kamchatka, eastern Russia. It occurs as small inclusions (up to 300 μm)
in isoferroplatinum grains. The crystal structure of cuproiridsite has not been solved whereas
Furubayashi et al. (1994) solved the crystal structure of the synthetic analogue. The name is after its
chemical composition.

403

404 **Cuprokalininite** $- CuCr_2S_4$

Cuprokalininite has been recently described by Reznitsky et al. (2011) from the Pereval 405 marble quarry, southern Baikal region, Russia. It occurs as euhedral {111} and {100} crystals, up to 406 407 200 µm in size, associated with quartz, Cr-V-bearing tremolite, Cr-V-bearing diopside, mica, calcite, and other rare minerals. Crystal structure was not solved, owing to the ubiquitous {111} 408 twinning of available crystals. Chemical analyses highlighted a significant V enrichment (up to 9.09 409 wt%, corresponding to 0.526 apfu), as substituent of Cr. Taking into account the physical properties 410 of this compound, two different structural models have been proposed, i.e. $Cu^{+}[Cr^{3+}Cr^{4+}]S^{2-}_{4}$ and 411 $Cu^{2+}Cr^{3+}_{2}S^{2-}_{4}$. At ambient conditions, the former phase is stable, whereas the latter is stable only 412 close to 0 K. According to Reznitsky et al. (2011), no indications of miscibility between kalininite 413 414 and cuprokalininite have been found. The name underlines that this mineral is the copper analogue of kalininite. 415

416

417 **Cuprorhodsite** $- CuRh_2S_4$

This mineral was first described by Rudashevsky et al. (1985) from the same occurrence of cuproiridsite, with which cuprorhodsite is strictly associated as micrometric grains in isoferroplatinum. The name is after its chemical composition. Cuprorhodsite forms an extensive solid solution with cuproiridsite and malanite (e.g., Garuti et al. 1995; Barkov et al. 1997). The 422 crystal structure of cuprorhodsite has not been solved, whereas Riedel et al. (1981) studied its423 synthetic analogue.

424

425 **Daubréelite** $- FeCr_2S_4$

426 Daubréelite was first described by Smith (1876) from the Coahuila meteorite, Bolsom de 427 Mapimí, Mexico, in association with troilite. Initially, daubréelite was described as a chromium sulfide owing to the small amount of available material and the difficulty of separating it from 428 troilite; two years later, Smith (1878) found more abundant material and was able to chemically 429 separate daubréelite from troilite. Consequently, he succeeded in describing the correct chemical 430 formula of the new mineral. Since then, daubréelite has been found in a large number of metallic 431 meteorites. Owing to its typical occurrence, daubréelite was named after the French scientist 432 Gabriel Auguste Daubrée (1814-1896), who worked extensively with meteorites. Crystal structure 433 was solved by Lundqvist (1943) and since then several crystal structure studies on synthetic 434 FeCr₂S₄ have been performed. EXAFS spectra provide evidences that daubréelite is a normal spinel 435 (Charnock et al. 1990). 436

437

438 **Ferrorhodsite** – FeRh₂S₄

Ferrorhodsite is the Fe analogue of cuprorhodsite; it has been described by Rudashevsky et al. (1998) from the Chad massif and the Konder alkaline-ultramafic massif, Far-Eastern Region, Russia, as micrometer-sized inclusions (up to $50 \times 70 \ \mu\text{m}^2$) in isoferroplatinum. The name is after its chemical composition and relationship to cuprorhodsite. Crystal structure of natural material has not been solved, whereas the structure of synthetic FeRh₂S₄ was studied by Riedel et al. (1981).

444

445 **Fletcherite** $- CuNi_2S_4$

Fletcherite was found at the Fletcher mine, Reynolds County, Missouri, USA, and described
by Craig and Carpenter (1977). It has been named after the type locality. Fletcherite occurs as
crystals ranging in size between 1 and 200 μm, disseminated in bornite, chalcopyrite, and digenite.
Chemical data indicate extensive Ni-Co substitution. Crystal structure was not solved.

450

451 Florensovite – $Cu(Cr_{1.5}Sb_{0.5})S_4$

Florensovite was described by Reznitsky et al. (1989) from the Pereval marble quarry, southern Baikal region, Russia. Up to now, this is the only known locality for this species. By analogy with the synthetic counterpart, it is assumed that Cu is monovalent, Cr is trivalent, and Sb is pentavalent. It forms a complete solid solution with kalininite, with a constant Cu:Sb atomic ratio of 2:1, related to the substitution $2Cu^+ + Sb^{5+} = 2Zn^{2+} + Cr^{3+}$. It does not form a solid solution with cuprokalininite (Reznitsky et al. 2011). Florensovite honours Nikolai Aleksandrovich Florensov (1909-1986), Ukrainian geologist, for his contribution to the study of Siberian geology. The crystal structure of synthetic CuCr_{1.5}Sb_{0.5}S₄ has been solved and refined by Warczewski et al. (1997).

460

461 **Greigite** - FeFe₂S₄

The compound Fe₃S₄ was first described by Doss (1912) as melnikovite and confirmed by 462 Polushkina and Sidorenko (1963, 1968) as cubic Fe₃S₄, identical to the material described by 463 Skinner et al. (1964) under the name greigite. The latter authors reported the occurrence of this 464 465 sulfospinel from drill cores recovered in Tertiary lacustrine sediments from the Kramer-Four 466 Corners area, San Bernardino County, California, USA. Greigite was named after Joseph Wilson Greig (1895-1977), a mineralogist and physical chemist at the Pennsylvania State University, USA. 467 In 1968, because the name melnikovite was commonly used to designate a wide variety of poorly 468 crystalline iron sulphides, the then CNMMN decided to retain the name greigite (Fleischer 1969). 469 The crystal structure has been reported in the type description (Skinner et al. 1964). Greigite is an 470 471 inverse spinel and it is the sulfur analogue of magnetite (Vaughan and Craig 1985).

472

473 **Indite** $- \operatorname{FeIn}_2S_4$

Indite was described from the Dzhalinda tin deposit, Far-Eastern Region, Russia, as grains less than 2 mm (rarely up to 0.5 mm) by Genkin and Murav'eva (1963). It has been named after its chemical composition. The crystal structure of indite was not solved but X-ray diffraction data point to its analogy with synthetic $FeIn_2S_4$, whose crystal structure was reported by Hahn and Klinger (1950).

479

480 **Kalininite** – $ZnCr_2S_4$

Kalininite has been described by Reznitsky et al. (1985) in diopside-quartz-calcite rocks of the Slyudyanka complex exploited in the Pereval marble quarry, southern Baikal region, Russia. Up to now, this is the only known locality in which kalininite has been reported. It occurs as irregular slag-like aggregates up to 0.5 mm in garnet and pyroxene, associated with karelianite-eskolaite. It has been named after the mineralogist and petrologist Pavel Vasil'evich Kalinin (1905-1981), investigator of the southern Baikal region. The crystal structure of $ZnCr_2S_4$ has been solved only on synthetic material (i.e., Raccah et al. 1966; Wittlinger et al. 1997).

488

489 **Linnaeite** $- CoCo_2S_4$

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Known since long time with different names (e.g., *koboldine*, *kobaltkies*), linnaeite was the first sulfospinel to be recognized as a mineral species (Brault 1746) and it was reported with its current name by Haidinger (1845), in honour of the Swedish taxonomist, botanist, physician, geologist, and zoologist Carl Nilson Linnæus (1707-1778). Its type locality is considered the ironcopper-REE mine of Bastnäs, Västmanland, Sweden. Its crystal structure was solved and refined by Menzer (1926) and, successively, by Lundqvist and Westgren (1938).

496

497 **Malanite** $- CuPt_2S_4$

Malanite was first described by Yu et al. (1974) during a preliminary study of Chinese 498 platinum minerals occurring in peridotitic rocks but it was not submitted to the IMA approval. In 499 the original description, unit-cell parameter and chemical formula were given as a = 6.03 Å and 500 (Cu,Pt,Ir)S₂, respectively. Peng et al. (1978) re-indexed the powder data on the basis of a cubic cell 501 with a = 10.0 Å, suggesting the chemical formula Cu(Pt,Ir)₂S₄. Yu (1981) re-examined malanite 502 and a mineral previously described as dayingite (Yu et al. 1974), finding the identity between these 503 two phases, with the latter being a cobalt-rich variety of malanite. Finally, malanite was submitted 504 505 and approved by the Commission on New Minerals and Mineral Names, IMA and described by Yu (1996). The name is after the type locality, the Malan Valley, Chengde Prefecture, Hebei Province, 506 China. In addition to the continuous solid solution with cuproiridsite and cuprorhodsite, malanite 507 can form a solid solution with Ni-Co sulfospinels, i.e. carrollite, CuCo₂S₄, and fletcherite, CuNi₂S₄ 508 (Barkov et al. 1997). Structural data are not available. 509

510

511 **Polydymite** $- NiNi_2S_4$

512 This relatively common nickel sulfospinel was described by Laspeyeres (1876) from the 513 Grünau mine, Siegerland, Germany. The name is after the Greek words $\pi o\lambda v \zeta$, many, and $\delta i \delta v \mu o \zeta$, 514 twin, owing to the widespread twinning shown by its crystals. The crystal structure was solved 515 using synthetic NiNi₂S₄ by Lundqvist (1947).

516

517 **Siegenite** - CoNi₂S₄

Dana (1850) first reported the name siegenite, after its type occurrence in the Siegen District, Westphalia, Germany; previously, it had been indicated as *kobaltnickelkies* by Rammelsberg (see Palache et al. 1944). The chemical composition of siegenite lies along the Co–Ni join, between ideal polydymite, NiNi₂S₄, and linnaeite, CoCo₂S₄; natural siegenite can contain minor Cu and Fe (e.g. Zakrzewski 1984). Usually, siegenite lies on the Ni-rich side of the Ni:Co = 1:1 point, along the Co–Ni join (Tarr 1935; Vokes 1967) but Co-rich siegenite has been reported

2/19

524 (Petruk et al. 1969). The crystal structure of synthetic $CoNi_2S_4$ was studied by Huang and Knop 525 (1971).

526

527 **Trüstedtite** – NiNi₂Se₄

Trüstedtite was first reported by Vuorelainen et al. (1964) from the Kitka river valley, Kuusamo, Finland, where it occurs in uranium-bearing calcite veins embedded in sills of basaltic rocks. It probably forms a solid solution with polydymite. Trüstedtite was named in honour of Otto Trüstedt (1866-1929), Finnish mining engineer, whose work on prospecting methods lead to the discovery of the Outokumpu ore deposit, Finland. Structural data are not available.

533

534 **Tyrrellite** $- CuCo_2Se_4$

Tyrrellite was first described by Robinson and Broker (1952) as an unnamed mineral from 535 Eagle Claims, Beaverlodge Lake area, northern Saskatchewan, Canada. Later, the authors 536 informally named it tyrrellite, in honour of Joseph Burr Tyrrell (1858-1957), geologist of the 537 Geological Survey of Canada who first study the Beaverlodge area. Harris (1970) gave new data of 538 539 tyrrellite using specimens from the type locality and from a new occurrence at Bukov, Moravia, Czech Republic. The crystal structure of tyrrellite has been solved by Yang et al. (2007). The 540 541 structural study provided the basis for a redefinition of the chemical formula, Cu(Co,Ni)₂Se₄, rather 542 than the previously suggested (Cu,Co,Ni)₃Se₄ (Machatski and Stradner 1952). Cu is hosted in tetrahedral coordination, whereas Co occurs at the octahedral site. 543

544

545 Violarite – $FeNi_2S_4$

Clarke and Catlett (1889) described a ferroan variety of polydymite from the Vermilion 546 mine, Sudbury, Ontario, Canada; Lindgren and Davy (1924) recognized the same mineral from the 547 Key West mine, Nevada, USA, and the senior author remarked the differences between this ferroan 548 "polydymite" and polydymite from the German type locality. Consequently, he proposed the 549 550 institution of the new mineral species violarite; the name is from the Latin violaris, recalling the violet grey color shown by this mineral in polished section. Since then, violarite has been found in 551 several localities world-wide. ⁵⁷Fe Mössbauer spectroscopy indicates an octahedral coordination of 552 Fe^{2+} , although a possible contribution from tetrahedral iron seems to be possible (Vaughan and 553 554 Craig 1985). This result agrees with the neutron powder diffraction study of iron and nickel ordering in synthetic FeNi₂S₄ performed by Tenailleau et al. (2006), confirming the octahedral 555 556 coordination of Fe and the inverse type structure of this compound.

558 **Xingzhongite** – PbIr₂S₄

The history of xingzhongite is troubled. First described by Yu et al. (1974) from an 559 unknown Chinese locality, xingzhongite was reported as a cubic or pseudocubic minerals with a =560 8.72 Å and ideal chemical formula (Ir,Cu,Rh)S. According to Fleischer et al. (1976), the ideal 561 formula could be written as (Cu,Rh,Pb)IrS₂. Peng et al. (1978) re-indexed the cubic cell obtaining a 562 parameter a = 10.10 Å, whereas the Institute of Geochemistry, Chinese Academy of Science (1981) 563 reported new chemical analyses and a cubic cell with a = 9.970 Å, space group $Fd\overline{3}m$. According 564 to Dunn et al. (1984), the new chemical data recalculates, on the basis of 4 S atoms, to 565 $(Pb_{0.37}Cu_{0.35}Fe_{0.17})_{\Sigma=0.89}(Ir_{1.33}Rh_{0.41}Pt_{0.29})_{\Sigma=2.03}S_4$, ideally PbIr₂S₄. In addition, the X-ray powder 566 diffraction patterns collected on the Pb-free and the Pb-bearing phases are different. Consequently, 567 the identity of the Pb-bearing species with the mineral described earlier with the same name is 568 questionable. The confusion about the identity of xingzhongite is confirmed by two studies 569 describing the occurrence of this mineral with the formula proposed by Yu et al. (1974) from New 570 Caledonia (Augé 1988) and the Finero ultrabasic complex, Italy (Garuti et al. 1995). It should be 571 noted that this phase seems to correspond to cuproiridsite. 572

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- 574

Implications

In the systematic study of the various mineral classes, the IMA-CNMNC solicited over the 575 576 years *ad-hoc* subcommittees to prepare comprehensive reviews on several groups or supergroups of minerals, such as amphiboles, epidotes, zeolites, micas, sulfosalts, etc., aiming at making order on 577 the nomenclature and at establishing general rules for the validity of species within each group. Due 578 to their basic stoichiometry ($AB_2\phi_4$, with $\phi = O^{2-}$, S^{2-} , Se^{2-}), spinels seem to display a quite simple 579 crystal-chemistry; on the contrary, they display a wide chemical variability, with solid solution 580 series between different endmembers. Owing to the outstanding position of spinel-type structure in 581 582 many branches of Science (e.g., mineralogy, petrology, ore geology, gemology, mineral physics, solid state physics), and due to the lack of any official IMA-CNMNC report on spinels, this short 583 review of the state-of-the-art of currently valid mineral species could be useful as a base for future 584 crystal-chemical investigations. 585

586

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978 **Table captions**

- Table 1. Oxide spinels: valid mineral species, ideal chemical compositions, and selected structuraldata.
- Table 2. Sulfo- and selenospinels: valid mineral species, ideal chemical compositions, and selected
 structural data.
- 983

984 **Figure captions**

- Figure 1. Specimens of minerals with spinel-type structure (a) The oxide spinel magnetite, as
 octahedral crystals with feldspar, from Cerro Huañaquino, Potosí Department, Bolivia. (b) The
 sulfospinel carrollite, cube-octahedral crystal with calcite from Kambove District, Katanga Copper
 Crescent, Katanga, Democratic Republic of Congo.
- Figure 2. Spinel structure, with the cubic cell outlined. Octahedral and tetrahedral sites are shownin dark grey and light grey, respectively.

Table 1. Oxide spinels: valid mineral species, ideal chemical composition and selected structural

993 data.

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2-3 Spinels ($A^{2+}B^{3+}_{2}O_{4}$)											
	Mineral species	Chemistry	<u>a (Å)</u>	<t–o> (Å)</t–o>	<m–o> (Å)</m–o>	Ref.					
	Gahnite	ZnAl ₂ O ₄	8.085	1.953	1.912	[1]					
$D = \Lambda I^{3+}$	Galaxite	MnAl ₂ O ₄	8.181	1.991	1.927	[2]					
D – Al	Hercynite	FeAl ₂ O ₄	8.154	1.968	1.928	[3]					
	Spinel	MgAl ₂ O ₄	8.083	1.914	1.931	[4]					
	Chromite	FeCr ₂ O ₄	8.376	1.997	1.994	[5]					
0.	Cochromite	CoCr ₂ O ₄	8.335	1.963	1.996	[6]					
$B = Cr^{3+}$	Magnesiochromite	MgCr ₂ O ₄	8.333	1.965	1.995	[5]					
	Manganochromite	MnCr ₂ O ₄	8.437	2.031	1.998	[7]					
	Zincochromite	ZnCr ₂ O ₄	8.327	1.967	1.991	[8]					
	Cuprospinel	CuFe ₂ O ₄	8.394	1.890	2.057	[9]					
	Franklinite	ZnFe ₂ O ₄	8.442	1.978	2.027	[10]					
р г 3+	Jacobsite	MnFe ₂ O₄	8.496	2.001	2.035	[11]					
B = Fest	Magnesioferrite	MgFe ₂ O ₄	8.384	1.910	2.043	121					
	Magnetite	FeFe ₂ O ₄	8.397	1.886	2.061	[13]					
	Trevorite	NiFe ₂ O ₄	8.347	1.877	2.048	[14]					
	Coulsonite	FeV ₂ O ₄	8.453	1.991	2.025	[15]					
$B = V^{3+}$	Magnesiocoulsonite	MgV ₂ O ₄	8.42	1.954	2.032	[16]					
	Vuorelainenite	MnV_2O_4	8.52	2.041	2.023	[17]					
	4	-2 Spinels (A	A ⁴⁺ B ²⁺ 2O ₄)							
	Mineral species	Chemistry	<u>a (Å)</u>	<t–o> (Å)</t–o>	<m–o> (Å)</m–o>	Ref.					
	Ahrensite	SiFe ₂ O ₄	8.234	1.652	2.137	[18]					
$B = Fe^{2+}$	Brunogeierite	GeFe ₂ O ₄	8.413	1.771	2.132	[19]					
	Ulvöspinel	TiFe ₂ O ₄	8.532	2.006	2.046	[20]					
$B = Ma^{2+}$	Qandilite	TiMg ₂ O ₄	8.438	1.980	2.025	[21]					
	Ringwoodite	SiMg ₂ O ₄	8.071	1.665	2.066	[22]					
$B = Mn^{2+}$	Filipstadite	$(Sb_{0.5}Fe_{0.5})Mn_2O_4$	8.463 (x 3)	2.029 ¹	2.076 ¹	[23]					

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996 [1] Ardit et al. 2012;[2] Essene and Peacor 1983;[3] Lenaz and Skogby 2013; [4] Redfern et al.
997 1999; [5] Lenaz et al. 2004; [6] Garcia Casado and Rasines 1986; [7] Raccah et al. 1966; [8]
998 O'Neill and Dollase 1994; [9] Mexmain 1971; [10] Pavese et al. 2000; [11] Lucchesi et al. 1997;
999 [12] Andreozzi et al. 2001; [13] Fleet 1984; [14] Blesa et al. 1993; [15] Reuter et al. 1969; [16]
1000 Reuter et al. 1983; [17] Plumier 1962; [18] Yagi et al. 1974; [19] Welch et al. 2001; [20] Bosi et al.
1001 2009; [21] Wechsler and Von Dreele, 1989; [22] Hazen et al. 1993; [23] Bonazzi et al. 2013.

1002 Note: ¹ average bond distances of T and M sites weighted taking into account the different 1003 multiplicities of the individual sites (Bonazzi et al. 2013).

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Table 2. Sulfo- and selenospinels: valid mineral species, ideal chemical compositions, and selected
 structural data.

Sulfospinels											
	Mineral species	Chemistry	a (Å)	<t–s> (Å)</t–s>	<m–s> (Å)</m–s>	Ref.					
B = Co	Carrollite Linnaeite	$CuCo_2S_4$ $CoCo_2S_4$	9.464 9.401	2.164 2.198	2.302 2.260	[1] [2]					
<i>B</i> = Cr	Cuprokalininite Daubréelite Florensovite Kalininite	$\begin{array}{l} CuCr_2S_4\\ FeCr_2S_4\\ CuCr_{1.5}Sb_{0.5}S_4\\ ZnCr_2S_4 \end{array}$	9.810 9.976 9.993 9.974	2.260 2.325 2.288 2.325	2.377 2.403 2.429 2.402	[3] [4] [5] [6]					
B = Fe	Greigite	$FeFe_2S_4$	9.876	2.14	2.46	[7]					
<i>B</i> = In	Cadmoindite Indite	$CdIn_2S_4$ FeIn_2S_4	10.797 10.598	2.543 2.460	2.586 2.558	[8] [8]					
B = Ni <i>B</i> = PGE	Fletcherite Polydymite Siegenite Violarite Cuproiridsite Cuprorhodsite Ferrorhodsite Malanite	$CuNi_{2}S_{4}$ $NiNi_{2}S_{4}$ $CoNi_{2}S_{4}$ $FeNi_{2}S_{4}$ $CuIr_{2}S_{4}$ $CuRh_{2}S_{4}$ $FeRh_{2}S_{4}$ $CuPt_{2}S_{4}$	9.520 9.457 9.424 9.442 9.847 9.791 9.890 9.910	no data 2.211 2.189 2.172 2.303 2.272 2.295 no data	available 2.274 2.273 2.289 2.367 2.363 2.387 available	[9] [10] [11] [12] [13] [3] [3] [14]					
	Xingzhongite	Pblr ₂ S ₄	9.970	no data	available	[15]					
Selenospinels											
	Mineral species	Chemistry	a (Å)	<t–se> (Å)</t–se>	<m–se> (Å)</m–se>	Ref.					
<i>B</i> = Co	Bornhardtite Tyrrellite	CoCo ₂ Se ₄ CuCo ₂ Se ₄	10.2 9.988	no data 2.369	available 2.384	[16] [17]					
<i>B</i> = Ni	Trüstedtite	$NiNi_2Se_4$	9.94	no data	available	[18]					

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[1] Riedel and Horvath 1973; [2] Lundqvist and Westgren 1938; [3] Riedel et al. 1981; [4] Lo Presti
and Destro 2008; [5] Warczewski et al. 1997; [6] Wittlinger et al. 1997; [7] Skinner et al. 1964; [8]
Hahn and Klingler 1950; [9] Craig and Carpenter 1977; [10] Lundqvist 1947; [11] Huang and Knop
1971; [12] Tenailleau et al. 2006; [13] Furubayashi et al. 1994; [14] Yu 1996; [15] Institute of
Geochemistry, Chinese Academy of Science 1981; [16] Ramdohr and Schmitt 1955; [17] Yang et
al. 2007; [18] Vuorelainen et al. 1964.

- Figure 1. Specimens of minerals with spinel-type structure (a) The oxide spinel magnetite, as
 octahedral crystals with feldspar, from Cerro Huañaquino, Potosí Department, Bolivia. (b) The
 sulfospinel carrollite, as cube-octahedral crystal with calcite from Kambove District, Katanga
 Copper Crescent, Katanga, Democratic Republic of Congo.



Figure 2. Spinel structure, with the cubic cell outlined. Octahedral and tetrahedral sites are shownin dark grey and light grey, respectively.





