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Abstract: Minerals of the Zn-Cd-S-Se system that formed by moderately reduced ~800–850 °C combustion metamorphic (CM) alteration of marly sediments were found in marbles from central Jordan. Their precursor sediments contain Se- and Ni-enriched authigenic pyrite and ZnS modifications with high Cd enrichment (up to ~10 wt%) and elevated concentrations of Cu, Sb, Ag, Mo, and Pb. The marbles are composed of calcite, carbonate-fluorapatite, spurrite, and brownmillerite and characterized by high P, Zn, Cd, U, and elevated Se, Ni, V, and Mo contents. Main accessories are either Zn-bearing oxides or sphalerite, greenockite, and Ca-Fe-Ni-Cu-O-S-Se oxychalcogenides. CM alteration lead to compositional homogenization of metamorphic sphalerite, for which trace-element suites become less diverse than in the authigenic ZnS. The CM sphalerites contain up to ~6.7 wt% Se but are poor in Fe (means 1.4–2.2 wt%), and bear 100–250 ppm Co, Ni, and Hg. Sphalerite (Zn,Cd,Fe)(S,O,Se)cub is a homogeneous solid solution with a unit cell smaller than in ZnScub as a result of S2− → O2− substitution (a = 5.40852(12) Å, V = 158.211(6) Å³). The amount of lattice-bound oxygen in the CM sphalerite is within the range for synthetic ZnS1−xOx crystals (0 < x ≤ 0.05) growing at 900 °C.

Keywords: ZnS; sphalerite; würtzite; greenockite; trace elements; Mottled Zone; combustion metamorphism

1. Introduction

Various aspects of sphalerite geochemistry have received much attention in the literature ([1] and references therein). Most publications deal with sphalerite from economic Zn and Pb-Zn deposits. The mineralogy of sulfides (including ZnS modifications) is often of little interest for metamorphic petrologists because sulfides reequilibrate much more quickly than silicate minerals [2] and thus do not represent the peak metamorphic conditions. However, sulfide assemblages were recently reported [3] to store records of changes in metamorphic environments and regimes. Brown et al. [3] considered...
several isochemical changes of sulfides for the case of blueschist and eclogite metamorphic rocks. They included (i) polymorphic transition of a phase, with no reactions between phases; (ii) composition changes of solid solutions in response to \( P-T \) changes; (iii) homogenization of a multiphase assemblage to a single phase (complex solid solution) upon heating; and (iv) breakdown of a complex phase to a multiphase assemblage of the same bulk composition upon cooling. The compositions of sulfides may also be interesting in terms of impurities and new mineral species: \( P-T \) changes and mineral growth in prograde reactions may be responsible for extremely high contents of impurities and rare minerals in high-grade metamorphic assemblages. Under these conditions, sulfides, unlike other rock-forming and accessory minerals, can accommodate chalcophile minor (Cu, Ni, Co, Zn, As) and trace (Cd, Hg, Ti, Sb, Se, Pb, Mo, Bi, Ag, Re) elements. This effect is especially impressive in Fe-poor high-grade marbles with rock-forming calcite and Ca(Mg) silicates \([4-16]\). They are specifically calcareous rocks produced by high-temperature low-pressure combustion metamorphism (CM) of marine chalky-marly sediments with variable percentages of phosphorite and clayey components and different abundances of minor and trace elements (P, S, Se, F, Sr, Ba, V, Cr, Ni, Cu, Ag, Zn, U) \([4,14,17-22]\). The CM marbles of central Jordan were derived mainly from the Belqa Group Maastrichtian–Early Eocene marly chalks. These bioproductive sediments have very high contents of redox-sensitive elements (mainly Zn, Cd, U, as well as Ni, V, Mo, Cu, and Se) and store disseminated organic matter (OM) with 9–11 wt% of sulfidic sulfur \([4,14]\). The marbles formed by spontaneous ignition and combustion of OM and by annealing of the Belqa Gr. sediments at 700–850 °C at a shallow depth.

The CM rocks of the area have uniform rock-forming mineralogy with predominant calcite, less abundant spurrite and apatite supergroup minerals, minor brownmillerite, and scarce mayenite supergroup minerals. The marbles are remarkable for unusual and abundant accessory mineralization, with numerous Zn minerals. They contain primary sphalerite, zincite, tuluilite, and Zn-rich periclase and secondary qatranaite (\( \text{CaZn}_2(\text{OH})_6 \cdot 2\text{H}_2\text{O} \)); diverse Cd compounds; various Ca uranates and their hydrated derivates; as well as Se-rich Ni and Ag chalcogenides. Zinc was revealed as an important impurity in primary brownmillerite, periclase, (Ca,Cd)O, mayenite and spinel supergroup minerals, and in secondary Ca silicate hydrates (CSHs) \([4,14,16,18-20,22-24]\).

This study focuses on high-temperature (800–850 °C) spurrite-fluorapatite CM marbles from a site in central Jordan locally known as Tulul al Hammam. The rocks bear unique Zn mineralization, with Zn- and/or Cd-bearing oxides, abundant sphalerite, and sporadic greenockite crystals. Speculation about the maximal storage capacity of the sphalerite structure relative to a set of chalcophile elements is mainly based on the respective high-temperature (\( T \geq 700 \) °C) phase diagrams, but too little is known about the real trace element composition of high- and ultra-high-temperature natural sphalerites because of their extremal rarity. The purpose of the current contribution was to provide for the first time analytical data characterizing the main and trace elements’ composition as well as the structure of sphalerites from the Tulul al Hammam CM marbles with high Cd, Se, V, Cr, Ni, Cu, Ag, Zn, and U enrichment \([4,14,17-22]\). The goals of the study were (i) to obtain first constraints for (Zn\(_{1-x}\)Me\(_x\))\((S\(_{1-y}\)As\(_y\))\) complex solid solutions that formed in natural high-temperature and ambient-pressure environments; (ii) to reveal relationships in trace-element (TE) compositions of CM sphalerite and the primary TE hosts from precursor sediments; (iii) to constrain trends of TE fractionation into CM sphalerite; and (iv) to understand the reasons for minor- and trace-element substitutions in ZnS\(_{\text{cub}}\) during natural high-temperature low-pressure alteration.

A combination of several advanced analytical techniques was applied to better resolve lattice-hosted elements and those in nano- and microinclusions \([1]\), epitaxial multi-phase ‘sandwiches’ (ZnS\(_{\text{cub}}\), ZnS\(_{\text{hex}}\), CdS, ZnO) \([25-29]\), and in other defects, which may be problematic to discriminate even at the scale of an electron microprobe beam. CM sphalerite crystals were characterized by electron probe microanalyses (EPMA), scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS), elemental mapping, laser-ablation inductively coupled plasma mass spectrometry (LA-ICPMS), single-crystal X-ray diffractometry (XRD), and single-crystal Raman spectroscopy.
2. Geological Background

The CM rocks of the Daba-Siwaqa complex (Mottled Zone, central Jordan) known under a local name of varicolored marbles bear diverse Zn mineralization together with various Ca-U(VI) oxides and Cd-rich compounds [18–20,22]. The rocks were derived from marine sediments of the Belqa Group cropping out ubiquitously in the area (Figures 1 and 2). The sediments were deposited at shallow sea depths in a stable highly productive shelf environment between the Late Cretaceous and the Early Eocene (ca. 90–50 Ma ago) [4,14,18,30,31]. Their gentle folding and faulting were mostly related to continued tectonic movements along the Dead Sea-Jordanian Transform located ~60 km to the west of Daba-Siwaqa [31]. The organic-rich sediments were uplifted in the Quaternary and became exposed to spontaneous oxidation and in situ combustion of the hosted bitumen and disseminated sulfides within the tectonically disturbed zones. For details of the local geology, see [17,18,32].

In many outcrops, marbles are rather fresh and preserve the original lamination of the precursor sediments (Figure 3A). Fresh marbles rich in disseminated sulfides are black, while the altered varieties,
as well as those enriched in fresh brownmillerite and/or Ca-ferrites, are brown; strongly altered marbles are pale red or pink. Green marbles are rich in fluorapatite and/or fluorellestadite (Figure 3C,D). Fresh samples often show thin (≤3 cm) bands of contrasting colors that reflect an uneven distribution of sulfur-rich organic matter (±sulfides) and phosphates in the protoliths.

The type locality of CM sphalerite called Tulul al Hammam (Arabic for Pigeon’s Hill) (31°32′ N 36°12′ E) is situated in the northern Siwaqa area (Figure 1B) [18,32]. Varicolored CM marbles typically occur as lenticular bodies from a few meters to more than 60 m thick and build cliffs or hills. The marbles are derived from the Maastrichtian-Paleogene Muwaqqar Fm. chalk and marl enriched in phosphorous, organic matter, and trace elements, including Cd, Zn, and U. The whole sequence crops out along valleys (wadis), where bituminous chalk and marl lie under CM rocks, unconformable Pleistocene travertine, fluvial to lacustrine deposits, and Holocene to Present alluvium.

| Chemostratigraphy | Lithostratigraphy (Thickness) | Lithology | Depositional environments |
|--------------------|-------------------------------|-----------|--------------------------|
| Quaternary         |                               |           | Recent alluvial, wadi sediments (present day drainage network) |
| Holoocene          | Rounded to well-rounded gravels, sands and silts |           | +Hot-spring+, alluvial, mudflats |
| Pleistocene        | Travertine, poorly sorted angular to rounded clast gravels (mainly chert), sands and silts |           |
| Eocene             | Umm Rajm Chert Limestone Formation (30-45 m) | Chalky limestone, thin-bedded chert, packstone, grainstone, sparse phosphorite (fish fragments, gastropods, nannofossils, calcareous nanoplankton, silicoflagellates) | Deep-water pelagic, locally hypersaline, locally shallow lagoons |
| Tertiary           | Muwaqqar Chalk Marl Formation | Organic-rich chalky marl, chalk, limestone and chert concretions (bivalves, ammonites, gastropods, fish fragments, calcareous nanoplankton) | Deep-water pelagic ramp (locally small anoxic basins with density stratified water column) |
| Palaeocene          | Muwaqqar Chalk Marl Formation |           |                             |
| Maastrichtian       | Belqa Group                    |           | Shallow-water pelagic ramp, oyster bioherms on inner ramp, stagnant bottom: winnowed phosphorite |
| Campanian           | Qatrana Phosphorite Mb.         | Phosphorite, chert, chalk, chalky marl, oyster-rich coquina and bioherms (bivalves including large oysters, gastropods, fish and reptile fragments, ammonites, siliciflagellates, radiolaria, calcareous nanoplankton, foraminifera) | Shallow-water, pelagic inner ramp |
| Cenomanian          | Báliyya Coquina Mb.             |           | Pelagic ramp (mid-to inner), shallow shoreline |
|                    | Sultani Phosphorite Mb.         |           |                             |
| Ammonian            | Anman Silicified Limestone Formation | Chert, microcrystalline limestone, chalky marl, sparse phosphorite, oyster-rich coquina (bivalves including oysters, sparse ammonites, fish and reptile fragments, siliciflagellates, radiolaria) | Shallow-water, pelagic inner ramp |
| Cretaceous          | Wadi Umm Ghudran               | Chalk, thin-bedded chert, sparse phosphorite, dolomitic grainstone (bivalves, gastropods, fish fragments, calcareous nanoplankton) | Pelagic ramp (mid-to inner), shallow shoreline |
| Turonian            | Wadi As Sir Limestone          | Limestone, wackestone, packstone, sparse ooidal grainstone, chert nodules (bivalves, rudists, gastropods, foraminifera) | Rimmed shallow carbonate shelf, rudist patch reefs, shoaling inner shelf |

**Figure 2.** Synthesised stratigraphic nomenclature: lithostratigraphy and lithology of central Jordan. Compiled data from [4,31]. Mb. = Member.
3. Materials and Methods

The initial scrutiny of about 60 Zn-enriched marble samples from the Tulul al Hammam quarries showed that approximately one sample per 10 contains different percentages of sphalerite and/or (Cd,Zn)(S,Se) solid solutions, besides predominant oxygen-bearing primary and secondary Zn minerals. Seven samples of ZnS-bearing marbles, with 230 to 1440 ppm Zn, Zn/Cd from 4.4 to 77, and 4 to 500 ppm Se (DT-20, DT-25, DT-26, TH-11, TH-52, TH-74, and TH-79) were selected for detailed analytical work (Table 1). The analyses were carried out mainly at the Analytical Center for Multi-Elemental and Isotope Research (Sobolev Institute of Geology and Mineralogy (IGM), Novosibirsk, Russia) and at the South Urals Federal Research Center of Mineralogy and Geoecology (SU FRC MG) (Miass, Russia).

Major elements in bulk samples of marbles and chalky sediments were analyzed by the solution ICP-OES technique on a Thermo Jarrell Intertechs IRIS Advantage atomic emission spectrometer (USA) at IGM (Novosibirsk). The preconditioning procedure included fusion of powdered whole rock samples with lithium borate as in [33].

Trace elements in bulk samples of marbles and chalky sediments were determined by ICP-MS on an Agilent 7700x spectrometer (USA) at the SU FRC MG (Miass, Russia). For this, 50-mg specimens were digested in a mixture of 2 mL 69% HNO₃, 6 mL 30% HCl, and 2 mL of 40% HF in closed Teflon bombs using a Berghof SpeedWave microwave digestion system. The procedure was run in steps, programmed to a temperature of 180 °C and a ramp time of 5 min at step 1 and 180 °C, 5 min hold time, a constant power of 500 W, and a pressure of 20 bar at step 2. Then, the residue was re-dissolved in 5 mL HCl (1:1 V/V) and evaporated. Finally, the residue was dissolved in 10 mL of HNO₃ (20%; 1:5 V/V) and the solution was heated at 150 °C for 30 min.
Table 1. Trace-element compositions of sphalerite-bearing CM marbles, Tulul al Hammam area (Daba-Siwaqa complex), and their sedimentary protoliths (‘oil shales’) of the Muwaqqar Chalk Marl Formation (ppm).

| Element | DT-20 | DT-26 | DT-25 | TH-11 | TH-74 | TH-52 | TH-79 | TH-72 | JRD10-12E | DOS-1 | OSB | JRD10-14 |
|---------|-------|-------|-------|-------|-------|-------|-------|-------|-----------|-------|-----|----------|
| V       | 321   | 186   | 1152  | 130   | 52.0  | 235   | 55.0  | 457   | 499       | 357   | 186 | 338      |
| Cr      | 422   | 984   | 1880  | 119   | 36.3  | 71.0  | 98.0  | 579   | 266       | 412   | 356 | 452      |
| Mn      | 22.9  | 40.0  | 40.7  | 30.0  | 80.0  | 30.0  | 80.0  | na    | 30.0      | 19.5  | 32.0 | na        |
| Co      | 1.65  | na    | 2.16  | na    | na    | na    | na    | 9.68  | 2.44      | 4.10  | 5.12 |          |
| Ni      | 273   | 290   | 684   | 119   | 115   | 103   | 158   | 457   | 335       | 256   | 93.0 | 182      |
| Cu      | 164   | 126   | 329   | 28.1  | 18.8  | 25.6  | 36.8  | 220   | 50.0      | 104   | 67.0 | 77.9      |
| Zn      | 1519  | 1440  | 1091  | 470   | 333   | 329   | 231   | 1437  | 2321      | 1498  | 632 | 428      |
| Ga      | 2.17  | 3.89  | 7.20  | 1.50  | 2.80  | 1.49  | 2.32  | 2.80  | na        | 8.78  | 8.60 | na        |
| Ge      | na    | <0.20 | na    | <0.20 | 0.35  | 0.34  | 0.60  | 0.22  | na        | 0.53  | <0.20 | na        |
| As      | 24.2  | 30.5  | 34.4  | 11.9  | 81.9  | 23.9  | 14.9  | <6.0  | 145       | 16.0  | 21.1 | 22.0      |
| Se      | 38.4  | 181   | 503   | 6.50  | 4.00  | 6.31  | 13.9  | 595   | na        | 94.9  | 32.5 | na        |
| Sr      | 1271  | 1360  | 1349  | 968   | 967   | 1044  | 1565  | 1590  | 462       | 603   | 683 | 692      |
| Y       | 41.8  | 33.0  | 46.4  | 25.8  | 13.0  | 8.60  | 8.30  | 26.1  | na        | 27.6  | 13.2 | na        |
| Zr      | 19.3  | 59.0  | 35.3  | 21.2  | 20.7  | 21.2  | 33.6  | 67.0  | na        | 34.2  | 52.9 | na        |
| Nb      | 0.80  | 1.88  | 0.80  | 0.90  | 0.90  | <0.2  | 0.80  | 0.90  | na        | 0.73  | 5.70 | na        |
| Mo      | 9.78  | 31.8  | 70.3  | 12.6  | 3.20  | 5.30  | 1.50  | 6.04  | 803       | 178   | 70.9 | 951      |
| Ag      | na    | na    | 8.10  | 4.60  | 42.6  | <1.9  | 5.40  | 16.9  | na        | na    | na   | na        |
| Cd      | 60.9  | 39.0  | 41.4  | 28.2  | 75.0  | 25.9  | 3.00  | 697   | 98.2      | 224   | 69.0 | 85.3      |
| Sb      | 5.11  | na    | 12.5  | <2.7  | <2.7  | 4.40  | 4.20  | 11.2  | 18.74     | na    | na   | 6.93      |
| Ba      | 136   | 171   | 424   | 253   | 212   | 472   | 190   | 134   | 40.5      | 58.1  | 45.0 | 43.1      |
| Hg      | 0.007 | 0.003 | 0.003 | na    | na    | na    | na    | <0.002| na        | 0.014 | 0.025| na        |
| Pb      | 2.00  | 4.50  | 0.22  | 0.80  | 1.40  | 1.60  | 1.20  | 14.5  | 5.53      | 12.0  | 4.90 | 6.94      |
| Th      | 0.31  | 0.76  | 0.50  | 4.00  | 2.90  | 4.90  | 6.70  | 7.30  | 1.79      | 1.98  | 4.40 | 2.23      |
| U       | 24.0  | 24.0  | 15.1  | 9.10  | 6.20  | 3.90  | 3.90  | 24.0  | 134       | 36.6  | 14.1 | 455      |
| Zn/Cd   | 24.9  | 34.9  | 26.4  | 16.7  | 4.4   | 12.7  | 7.70  | 2.06  | 23.6      | 6.7   | 9.2  | 5.0       |

ICP-MS data. na = not analysed. Te contents are 0.35 ppm in sample DT-25 and <0.056 ppm in other samples; Tl, Sn, and Bi contents are below detection limits: <0.004 ppm Tl; <0.20 ppm Sn; <0.002 ppm Bi. Analyses of some samples were partly published before: TH-11, TH-72, and TH-74 in [18,19]; and DOS-1 and OSB in [14]. * TH-72 is a reference sample with abundant Zn-bearing oxides. ** after [4].
After cooling at room temperature, the solution was poured into 100-mL volumetric flasks and then filled with ultrapure water till the final designed volume for analysis. The quality control and quality assurance procedures included processing and analysis, at each batch, of two blanks and the BCR-2 certified reference material (NIST, USA). Minor and trace elements were quantified using 5-point daily calibration. The analyses were run in triplicate, and the results differed for less than 5%. Two blanks were prepared and included 10 samples in each batch. The procedural blanks accounted for less than 1% of the element concentrations. Precision and accuracy were estimated to be 10–15 rel% for all elements. Method detection limits for trace elements were in the range 0.01–0.5 µg/L. The analytical reproducibility was monitored using the BCR-2 standard, in which the measured values were consistent with the certified ones, with extraction efficiencies ranging from 93% to 120%. The method was slightly modified after those reported in [34,35].

Bulk Hg contents in the marble samples were measured by flameless atomic absorption spectrometry (AAS) on a Lumex RA-915M Hg analyzer (Lumex Ltd., Saint Petersburg, Russia) with an RP-91C pyrolysis attachment. Prior to analyses, the rock samples were powdered in a mortar and homogenized. The technical specifications of the instrument allow special preconditioning of solid samples to be avoided. The national standard of soil (SDPS-3) certified for heavy metals and mercury was used to calibrate the spectrometer and to check the quality of analyses. Relative analytical errors were 20% ($p = 0.95$) for concentrations from $5 \times 10^{-7}$ to $2.5 \times 10^{-2}$ wt% [36].

Scanning electron microscopy (SEM) was applied to identify minerals and to characterize the phase distribution and morphology of Zn-bearing phases, based on energy-dispersive spectra (EDS), back-scattered electron (BSE) images, and elemental maps (EDS system). The measurements were performed at IGM (Novosibirsk) on a Tescan Orsay TESCAN MIRA 3LMU microscope (Tescan Orsay Holding, Brno, Czech Republic) equipped with an Oxford Instruments AZTec Energy XMax-50 microanalyses system (Oxford Instruments Nanaalysis, Abingdon, UK). Thin sections were repolished immediately before analyses, and fresh cleavage surfaces were sputter coated with ~15- to 25-nm carbon films for SEM examination. EDS analyses of minerals were run in a high-vacuum mode at an accelerating voltage of 20 kV, a beam current of 1.5 nA, and a live spectra acquisition time of 20 s. The following synthetic compounds, minerals, and pure elements were used as reference samples for the elements analysed: SiO$_2$ (Si and O), Al$_2$O$_3$ (Al), diopside (Mg and Ca), albite (Na), orthoclase (K), Ca$_2$P$_2$O$_7$ (P), BaF$_2$ (Ba and F), FeS$_2$ (S), Cr$_2$O$_3$ (Cr), CsRe$_2$Cl$_6$ (Cl), SrF$_2$ (Sr), Ti, Fe, Mn, Zn, Ni, Cu, V, Ag, Cd, and Se.

Matrix correction was done using the XPP algorithm (exponential model of Pouchou and Pichoir matrix correction), implemented in the software of the microanalysis system. Metallic Co served for quantitative optimization (normalization to beam current and energy calibration of the spectrometer) [37–39]. The detection limits (3σ value) were 0.10 wt% for K, Ca, Fe, and Ni; 0.15 wt% for Se, Cu, Ag, and Cd; and 0.40 wt% for O.

The variation coefficients that characterize the repeatability of a single determination were found to be ~0.9 rel% for EDS in the compositional range of the main mineral-forming components ([C] > 10 wt%); ~3 rel% for minor components (1 wt% < [C] < 10 wt%), and ~13 rel% for impurities (0.3 wt% < [C] < 1 wt%) [37]. EDS was chosen as the principal method for fast identification of mineral phases and determination of their major- and trace-element compositions. Scanning electron microscopy in the BSE mode and elemental mapping were used to characterize various texture aspects in sphalerite-bearing mineral intergrowths, with a special focus on inhomogeneities in sphalerite grains (zoning and mineral inclusions).

Electron probe microanalyses (EPMA). Mineral chemistry of sulfides was analyzed in >10-µm grains on a Jeol JXA 8100 electron microprobe microanalyzer (Jeol, Tokio, Japan) in C-coated polished thin sections, at an accelerating voltage of 20 keV, a beam current of 20 nA, and a peak counting time of 10 s. The compositions of sphalerite and wurtzite were determined with reference to standards: synthetic ZnS for S Kα and Zn Kα, CuFeS$_2$ for Fe Kα and Cu Kα, CdS for Cd Lα, InAs for In Lα and As Lα, ZnSe for Se Lα, Sb$_2$S$_3$ for Sb Lα, FeNiCo for Ni Kα, and PbTe for Te Lα. The detection
limits (3σ value) for the elements were 0.03 wt% for Ni; 0.06 wt% for S, As, In, Cd, and Sb; 0.09 wt% for Cu, Zn and Te; and 0.2 wt% for Se. The matrix correction using the ZAF algorithm (generalized algebraic procedure; assumes a linear relation between concentarion and X-ray intensity) [40] was applied to raw data prior to recalculation into elements. Analytical accuracy was within 2 rel% for [C] > 5 wt% elements, and about 5 rel% for [C] < 2 wt% elements.

LA-ICPMS. The trace-element chemistry of Zn and Fe sulfides was determined by laser ablation mass spectrometry with inductively coupled plasma (LA-ICPMS) at the SU FRC MG (Mass). Phalerite was analyzed in polished sections of three selected coarse-grained samples (marble samples DT-20 and DT-25), würtzite and pyrite (sediment sample DOS-1) preconditioned using the standard equipment, and following the standard protocol [41]. The texture of the samples was examined by SEM with a special focus on inhomogeneities in ZnS and FeS₂ crystals (zoning or mineral inclusions). The selected large (50–200 µm) sulfide crystals are chemically homogeneous and generally free from visible inclusions or signatures of alteration. The LA-ICPMS method was of limited applicability for sphalerites from other marble samples, because they were too small (within 20 µm across) and often enclosed extraneous phases. The concentrations of Zn and Fe determined by EDS and WDS were used as internal standards for the LA-ICPMS trace- and minor-element data.

The LA-ICPMS analysis was run on a NewWave Research UP-213 laser ablation system coupled with an Agilent 7700x (Agilent Technologies, Inc., Santa Clara, CA, USA) plasma mass spectrometer. The procedure was as in [42], with an Nd: YAG UV source, frequency quadruple (wavelength 213 nm) with fluence settings of 2.5–3.5 J/cm² for pyrite and 3.5–5.0 for sphalerite and würtzite, helium cell carrier gas, and a gas flow rate of 0.6–0.7 L/min. The mass spectrometer settings were as follows: 1550 W RF power; Ar as a carrier gas; a flow rate of 0.95 to 1.05 L/min; a plasma gas flow (Ar) of 15 L/min; and an auxiliary gas flow (Ar) of 0.9 L/min. Each analysis was performed with a laser spot size of 30–100 µm at a frequency of 10 Hz. Each sample was measured for 90 s (30-s background measurements plus 60-s analysis), with 5-s pre-ablation before each analysis and 30-s washout between the analyses. The mass spectrometer was tuned with NIST SRM-612 glass. The Th/U ratio is ~1. Production of molecular oxide species (i.e., ²³²ThO/²³²Th) was maintained at <0.2%. The monitored isotopes included ⁵¹V, ⁵³Cr, ⁵⁵Mn, ⁵⁷Fe, ⁵⁹Co, ⁶⁰Ni, ⁶⁵Cu, ⁶⁶Zn, ⁶⁹Ga, ⁷²Ge, ⁷⁵As, ⁷⁷Se, ⁹⁵Mo, ¹⁰⁷Ag, ¹¹¹Cd, ¹¹⁵In, ¹¹⁸Sn, ¹²¹Sb, ¹²⁵Te, ¹⁹⁷Au, ²⁰²Hg, ²⁰⁵Tl, ²⁰⁸Pb, and ²⁰⁹Bi. The element contents were calibrated against reference materials of USGS MASS-1 and USGS GSD-1g using ⁶⁶Zn as an internal standard for sphalerite and würtzite, and ⁵⁷Fe for pyrite, respectively [43,44]. All mass fractions for USGS MASS-1 and USGS GSD-1g were taken from the GeoReM base preferred values. The calibration standard was analyzed every 10–12 spots to account for the instrument drift. Data processing was carried out using the lolite software package [45].

A sphalerite grain of a complex composition (Zn,Cd,Fe)(S,O,Se) was analyzed by single-crystal X-ray diffractometry on an Oxford Diffraction Xcalibur Gemini diffractometer (Oxford Diffraction Ltd., Wroclaw, Poland), MoKα, λ = 0.71073 Å (Novosibirsk State University, Novosibirsk, Russia). Diffraction data were collected by scanning of the ω angle with a step of 1° per frame (ω scan technique). The data were processed in CrysAlis Pro 171.38.43d ( Rigaku-Oxford Diffraction Ltd., Oxfordshire, UK) [46]. Semi-empirical absorption correction was applied using the multi-scan technique.

X-ray powder diffraction analyses of bulk rock samples was performed on an XRD-6000 diffractometer (Shimadzu Corporation, Kyoto, Japan) (CuKα₁+₂ radiation with graphite monochromator), at 4° to 70° 2θ, at a step of 0.5°.

Raman spectra of high-quality sphalerite crystals (reference sample DT-20) were recorded on a Horiba Jobin Yvon LabRAM HR800 spectrometer (Horiba Jobin Yvon S.A.S., Lonjumeau, France). The spectra were excited with two laser lines: a 532-nm green line of a Thorlabs 50-mW power neodymium Nd:YAG laser working at double-harmonic frequency and a Kimmon 325-nm ultraviolet line (UV) of a He-Cd gas laser. The radiated laser power was attenuated with optical filters and the beam power incident onto the sample was about ~0.1 mW. The scattered light was recorded by a 1024-channel Peltier-cooled CCD detector (Andor, Oxford Instruments, international
company based in Belfast, Northern Ireland) in a region of 70 to 3800 cm\(^{-1}\) at a resolution of 2 cm\(^{-1}\). The excitation was with Olympus objectives at magnifications of \(\times 50\) (WD = 0.4 mm) and \(\times 100\) (WD = 0.2 mm) for the green line and with an Olympus objective at \(\times 10\) (WD = 8 mm) and a LOMO objective of \(\times 50\) (WD = 0.2 mm) for the UV line. The Raman spectra of the selected CM sphalerite crystal \((Zn_{0.96}Fe_{0.02}Cd_{0.02})(S_{0.94}O_{0.05}Se_{0.01})\) were recorded at different points of the DT-20 sample and deconvoluted into Voigt amplitude functions using the Model S506 Interactive PeakFit software (2002 Spectroscopy Software, Canberra Industries, Meriden, CT, USA) [47].

4. Results

4.1. Sedimentary Protoliths and Their TE Hosts

All Belqa Gr. lithologies in Levant east of the Dead Sea—Jordanian Transform have abnormal enrichment in redox-sensitive elements (RSEs) that largely exceed the absolute contents in most of the organic-rich sediments worldwide. Trace elements are especially abundant and diverse in immature organic-rich siliceous chalk (‘oil shale’) of the Maastrichtian-Paleocene Muwaqqar Chalk Marl Fm., a unit of the Belqa Gr., in central Jordan (Figure 2) [4,14,18–20,30,48–51]. The Muwaqqar Fm. ‘oil shales’ were deposited on the southern Neo-Tethys epicontinental shelf in a setting typical of pristine phosphorites, under anoxic/euxinic conditions during intense upwelling. Large amounts of degrading organic matter consumed oxygen from the water column, while reducing conditions were favorable for the accumulation of liptinitic OM, with its share in the chalks reaching 30% [30,48,52]. Redox-sensitive elements were brought to sediments mainly by a biogenic shuttle. The bulk organic matter consists of type I/I\(_I\) kerogen sulfurized during sulfate reduction. Sulfate-reducing bacteria tended to sulfurize the OM and finally facilitated prolific precipitation of authigenic sulfides, which accumulated Zn, Cd, Fe, Ni, Cu, Mo, and Se [4,14,19,51].

The RSE enrichment is the highest in the basins of western and central Jordan that underwent synsedimentary subsidence [4,30,48,53]. The Muwaqqar ‘oil shales’ from the Siwaqa area, with up to 23 wt% organic matter and 4.3 wt% total sulfur (mainly sulfidic), are remarkable for exceptionally high contents of phosphorus and RSE that reach 4695 ppm Zn, 2176 ppm U, 727 ppm V, 496 ppm Mo, 448 ppm Ni, 418 ppm Cr, and 225 ppm Cd. The mean contents of other trace elements are moderate or low: \(\leq 60\) ppm Ba, \(\leq 0.1\) ppm Bi, \(\leq 10\) ppm Co, \(\leq 35\) ppm Mn, \(\leq 65\) ppm Cu, \(\leq 8\) ppm Pb, and \(\leq 6\) ppm Sb (Table 1) [4,14,30,48]. Metals reside mainly in sulfides: Zn-Cd-(Cu) in sphalerite or/and würtzite and Fe-Ni-V-Cu-(Mo) and Se in pyrite. S-rich organic matter is an important carrier of Ni, V, and sometimes Cu [14]. These very rocks are the sedimentary protoliths of CM marbles with unique accessory U, Cd, Zn, and Ni mineralogy [4,7,9,10,14,18–20,22,23].

‘Oil shales’ found at the base and in the middle of the Muwaqqar Fm. section are grey laminated fine-grained mainly calcitic rocks with abundant shell clasts (Figure 4). Foraminifera occur mainly in organic-rich sediments with 10 to 20 wt% total organic carbon. The chalks contain a few percent to 10–15% biogenic carbonate-fluorapatite, minor percentages of clay minerals (smectite, illite, or rarer kaolinite), quartz occurring as clastic material and/or chalcedony-like matter, as well as opal-A, opal-CT, or microquartz derived from a diatomaceous precursor [14,54,55].

Opaque minerals in the the Muwaqqar Fm. ‘oil shales’ are authigenic sulfides: predominant würtzite, less-abundant sphalerite (both with 7.6–9.6 wt% Cd), and sporadic framboidal pyrite (Figure 4) [4,14,19,30]. Authigenic Cd-rich sphalerite and würtzite are much more abundant than pyrite, for three main reasons: (i) S-bearing ligands coordinating Cd and Zn in primary OM; (ii) high sulfur in OM; and (iii) low concentrations of reactive iron in bottom sediments [14]. The sulfides were described in detail in an earlier publication in the context of Zn and Cd accumulation in bioproductive carbonate sediments [14]. Here, we confine ourselves to a brief summary of their trace-element compositions. EPMA of many sphalerite and würtzite crystals (\(\leq 10\) \(\mu m\)) has revealed very high contents of impurities in hexagonal ZnS polymorphs: an average of 8.63 wt% Cd, 0.69 wt% Cu, 0.33 wt% Fe, and 0.43 wt% As (Table 2). LA-ICPMS was restricted to a few plates of würtzite larger than 20 \(\mu m\).
Authigenic würtzite has an anomalous TE composition: tens of thousand ppm for Cd; thousands ppm of Fe, Cu, As, and Sb; and hundreds ppm of Ni, Hg, Pb, Se, Mo, and Ag (Table 3). Authigenic pyrite contains tens of thousand ppm of Cu; thousands ppm of As, Se, Mo, and Ag; and hundreds ppm of Mn, Co, Zn, Pb, and Tl. These TE resources were redistributed and partitioned between newly-formed CM sulfides during high-temperature alteration of the ‘oil shales’.

Figure 4. Cd-würtzite, Cd-sphalerite, and associated minerals in bituminous phosphatic chalk (‘oil-shale’) of the lower Muwaqqar Chalk Marl Formation. (A) Platy Cd-rich würtzites clustered inside foraminiferal chambers in a biomicritic matrix composed of calcite, silica, disseminated organic matter, and pristine phosphorite. (B) Foraminifera chambers filled with S-rich solid organic matter (type-II kerogen). Cd-rich würtzites occur as platy crystals and microcrystals inside chambers. (C) Cd-rich würtzite microcrystals and framboidal pyrite in biomicritic matrix. (D) Micrometer platy Cd-rich würtzite crystallites intimately intergrown with diatom frustules and radiolaria spicules (opal-CT). (E) Simple twinned pseudooctahedral sphalerite. Optical images in plane-polarized light (A) and BSE images (B–E). Cal = calcite, OM = organic matter, Phs = phosphorite, Py = pyrite; Sp = sphalerite, Wur = wurtzite.

Table 2. Average composition of sphalerite and würtzite from sedimentary rocks (‘oil shales’) of the Muwaqqar Chalk Marl Formation (SEM-EDS and EPMA data, wt%).

| Mineral | Sphalerite | Würtzite |
|---------|------------|----------|
| Sample  | DOS and OSB | DOS | |
| DOS    | (n = 24) | | |
| Mean   | S | Min | Max | Mean | S | Min | Max |
| Zn     | 58.20 | 0.26 | 57.80 | 58.51 | 58.01 | 0.99 | 56.26 | 59.18 |
| Cd     | 9.12  | 0.24 | 8.84  | 9.45  | 8.63  | 0.76 | 7.63  | 9.96  |
Table 2. Average composition of sphalerite and würtzite from sedimentary rocks (‘oil shales’) of the Muwaqqar Chalk Marl Formation (SEM-EDS and EPMA data, wt%).

| Mineral | Sphalerite | Würtzite |
|---------|------------|----------|
| Sample  | DOS and OSB (n = 24) | DOS (n = 27) |
|         | Mean S Min Max | Mean S Min Max |
| Zn      | 58.20 0.26 57.80 58.51 | 58.01 0.99 56.26 59.18 |
| Cd      | 9.12 0.24 8.84 9.45 | 8.63 0.76 7.63 9.96 |
| Fe      | 0.27 0.25 <0.10 0.50 | 0.33 0.21 <0.10 0.70 |
| Cu      | <0.15 – <0.15 0.69 | 0.15 0.42 0.91 |
| S       | 32.08 0.06 31.99 32.15 | 32.04 0.16 31.82 32.33 |
| Total   | 99.67 99.70 | 99.70 99.70 |

Mn, Ni (<0.10 wt%), and Se (<0.15 wt%) are below detection limits. Würtzite also contains As (mean 0.43 wt%, S 0.18 wt%, min 0.21 wt%, max 0.74 wt%) and Sb (mean 0.13 wt%, S 0.05 wt%, min <0.09 wt%, max 0.20 wt%).

n = number of analyses, Mean = mean value, S = standard deviation, Min = minimum value, Max = maximum value.

Table 3. Average trace-element composition (ppm) of sphalerite from spurrite-fluorapatite marbles (Tulul al Hammam area), compared with Fe- and Zn sulfides from ‘oil shales’ (Muwaqqar Chalk Marl Formation). LA-ICPMS data.

| Rock Type | ‘Oil Shales’ | Spurrite-Fluorapatite Marbles |
|-----------|--------------|-------------------------------|
| Sample    | DOS-1 Pyrite 6 | DOS-1 Würtzite 5 | DT-20 Sphalerite 16 | DT-25 Sphalerite 3 |
| Mineral   | Element | V 1554 2.93 bdl bdl | Mn 647 7.3 1565 355 | Co 120 bdl 124 66 | Ni 4990 230 220 265 |
| n         | Cu 34,340 | 7760 11.1 26 | Ga bdl 202 0.45 7.9 | Ge 2.75 381 bdl bdl |
|           | bdl   | Se 1343 2255 bdl bdl | As 6535 282 4440 13,910 | Mo 1332 606 bdl bdl |
|           | Ag 1103 645 | 0.42 0.33 | Cd 114 66,200 18,100 9240 | In bdl 0.69 4.51 2.44 |
|           | 0.3   | Sb 41.2 2145 1.19 3.03 | Te bdl bdl bdl bdl | Au bdl bdl bdl bdl |
|           | bdl   | Te bdl bdl bdl | Hg bdl 345 132 226 | Tl bdl 5.2 0.9 |
|           | Pb 269  | 604 bdl bdl | Bi 5.5 5.3 bdl bdl | Hg bdl 345 132 226 |

bdl = below detection limit; n = number of samples. Concentration of Zn in pyrite is 280 ppm.

4.2. Zn-Rich Marbles: Occurrence, Rock Chemistry, and Mineral Assemblages

The Tulul al Hammam sphalerite-bearing marbles are varicolored (mostly dark-shaded), foliated, massive, and microcrystalline (≤50–200 µm). The amount of sphalerite (Figure 5; Table 4) varies from single ≤2–10 µm particles in slightly altered greenish marbles (samples labeled as TH) to clusters of numerous crystals reaching 200 µm in fresh deep-brown fluorapatite marbles (samples labeled as DT) (Figure 3). These metasedimentary rocks share similarity in bulk chemistry, with predominant CaO (51.5–55.0 wt%) and commensurate contents of SiO₂ and P₂O₅ (3.40–4.85 and 3.74–4.54 wt%, respectively). Loss on ignition (LOI) is 29.1 to 34.1 wt%, mainly due to CO₂. The contents of other major elements are quite low, being within 2.28 wt% Al₂O₃, 2.28 wt% Fe₂O₃, 0.65 wt% MgO, 0.21 wt% Na₂O, and 0.06 K₂O. Bulk sulfur (determined as SO₃) is commonly 0.4–0.5 wt%.
The DT samples (Table 1) stand out against similar marbles of the same locality in Zn enrichment times greater than in the TH samples (1091 to 1660 ppm against 230–470 ppm Zn) which include only sporadic fine grains of (Zn,Cd)S or (Cd,Zn)(S,Se) solid solutions. Other RSE concentrations in the DT samples are also relatively high and reach 1152 ppm V, 42.6 ppm Ag, 329 ppm Cu, 684 ppm Ni, 81.9 ppm As, 503 ppm Se, 70.3 ppm Mo, 75 ppm Cd, and 24.0 ppm U. Most of the samples with higher TE loading show an uneven distribution of Zn, Cd, Ni, Ag, U, and Se and enclose excretions of the corresponding phases (Figure 5A,C). In fact, the CM rocks display a snapshot of original TE hosts left by the annealing of sediments: OM, pyrite, and ZnS polymorphs.

**Figure 5.** Sphalerite from medium-temperature combustion metamorphic spurrite-fluorapatite marbles (Tulul al Hammam area, central Jordan). (A,B) Numerous large sphalerite crystals inside calcite-rich layer. (C–F) Tetrahedral or pseudo-octahedral sphalerite twins in a calcite matrix. Sample DT-25 (A), sample DT-26 (B), sample DT-20 (C–F). Optical images in plane-polarized light (D,F) and BSE images (A–C,E). Cal = calcite, Sp = sphalerite, Spu = spurrite.
Most of the studied marbles consist of ~75–90% calcite, up to 15% carbonate-fluorapatite, ≤5% spurrite (Ca₅(SiO₄)₂(PO₄)₂), and ≤3% brownmillerite (Ca₂Fe₁₋ₓAlₓO₅), as well as sporadic grains of Ca ferrites, mayenite supergroup minerals, Zn-rich periclase, tululite, and accessory phases of Zn, Cd, Ni, Cu, Ag, and U (Table 4). The spurrite and fluorapatite percentages are as high as ~15% in sample DT-25, which contains 10.03 wt% SiO₂ (Figure 5A). Fluorapatite from sulphide-rich layers in the marbles contains no more than 1.85 wt% SO₃, while average contents of SiO₂ are 4.7–6.5 wt%. Marbles with abundant Zn-bearing oxides contain fluorapatites enriched in both SiO₂ (5.9–7.8 wt%) and SO₃ (2.8–5.3 wt%) (Figure 6; Table 5).

Table 4. Mineral assemblages of Zn-enriched Jordanian combustion metamorphic rocks—phosphate marbles with primarily Zn-bearing oxide and sulphide mineralization, Tulul al Hammam area. EPMA, SEM EDS, and XRD data.

| Sample/Rock Type | Main Phases | Minor Phases | Accessory Phases | Alteration Products |
|------------------|-------------|--------------|------------------|--------------------|
| DT-20            | Calcite     | *Fluorapatite (SiO₂—4.49 wt%; SO₃—1.15 wt%) | Spurrite          | CSHs (trace), Chlormayenite, Portlandite (CaO(OH)₂), Si- and F-bearing hydrated CaO-UF₄ compounds |
|                  |             |              | Periclase (Zn, Cu, Ni-rich), (Ca₂Cr₃) |                    |
|                  |             |              | Brownmillerite (Cr, Ti, Zn-rich), Ca ferrite, Fe, Ni, Cu sulfides, Ca-Fe-SO₃ compounds, Cerianite (Cr₃TiO₅), Lime (CaO), Lakargite (Ca₃FeO) |                    |
|                  |             |              |                    |                    |
| DT-25            | Calcite     | *Fluorapatite (SiO₂—4.95 wt%; SO₃—1.85 wt%) | Brownmillerite (Ti, Zn, Cr-bearing) | Hydrocalumite, Ni- and F-bearing hydrated CaO-UF₄ compounds |
|                  |             |              |                    |                    |
| DT-26            | Calcite     | *Fluorapatite (SiO₂—4.30 wt%; SO₃—0.49 wt%) | Spurrite |                    |
|                  |             |              |                    |                    |
| TH-74            | Calcite     | *Fluorapatite (SiO₂—5.30 wt%; SO₃ < 0.3 wt%), Brownmillerite (Ce, Ti, Zn-bearing) |                    | CSHs (trace), Zeolites, Chlormayenite, Fe hydroxides, Gypsum, Portlandite, Carnotite (K₂(UO₂)₂V₂O₈·3H₂O), Tyuyamunite or Metatyuyamunite (Ca₂SiO₃V₂O₈·5–8H₂O), Steinkinite (Na₂(UO₂)₂V₂O₈·6H₂O), Si- and F-bearing hydrated CaO-UO₃ compounds, Plattnerite (?)(PbO₂), Crocite (PbCrO₄), Chromatite (CaCrO₄) |
|                  |             |              |                    |                    |

(3.8–5.3 wt%) (Figure 6; Table 5).
Fluorapatite marble

Zn—231 ppm; 
Cd < 3 ppm 
Zn/Cd > 77

In the samples DT-25 and DT-26, carbonate-fluorapatite was identified by Raman spectroscopy.

Figure 6. Phosphorus-rich part of the Si–P–S diagram showing the composition (in atoms per formula unit, apfu) of fluorapatite and fluorellestadite from CM marbles (Tulul Al Hammam area). In the samples DT-25 and DT-26, carbonate-fluorapatite was identified by Raman spectroscopy.
Zinc was detected in any sample. Frequently, Zn sulfide and oxide accessories are unevenly distributed (CaUO$_2$ (0.3–0.9 wt% ZnO), tululite (23.7 wt% ZnO on average), cassiterite, cerianite (Ce,Th)O$_2$, vorlanite (CaUO$_4$), and lakargiite (CaZrO$_3$)). Other accessory minerals are scanty lime (CaO), oldhamite (CaS), srebrodolskite, and Fe-Zn spinel (Table 8). Zincite was found only in sample DT-20 with the highest Zn contents, where it is restricted to sulfide-free layers.

The distribution of brownmillerite, the most common opaque mineral in the Tulul al Hammam marbles, is apparently controlled by uneven patterns of authigenic pyrite and clayey matter in primary sediments. Brownmillerite is the principal host of Fe$^{3+}$, Al, and Zn in low-Zn spurrite-fluorapatite-calcite layers where it contains up to 3.8 wt% ZnO. The Zn contents are similar (2.4–3.8 wt%) in brownmillerite from marbles rich in Zn-bearing oxides (zincite, tululite, Zn-rich periclase) but are below 0.5 wt% in that coexisting with sphalerite. Other Zn-bearing oxides found coexisting with sphalerite are Zn-rich periclase (22–23.5 wt% ZnO), scarce grains of Zn-bearing (Ca,Cd)O and Zn contents, where it is restricted to sulfide-free layers rearing numerous large sphalerite crystals. Sphalerite occurs in Zn-rich marbles as transparent ≤200 µm pseudo-octahedral simple twins or tetrahedral crystals of deep yellow-brownish colors (DT-20), subhedral grains (DT-26), or complex intergrowths and exsolution lamelli with Ni, Cd, Cu, and Ag sulfides and/or selenides (DT-25) (Figures 5, 7 and 8).

The marbles with the greatest TE loading (samples DT-20, DT-25 and DT-26) store a whole collection of mineralogical rarities (Tables 4 and 6–8). The rocks include diverse Fe, Ni, Cu, and Ag chalcogenides that coexist with sphalerite and occur as complex micrometer aggregates exsolved from primary-high-temperature complex sulfides, sulfo-selenides, and/or oxychalcogenides. They are rassvumite (with ~3 wt% Ti and 1.1 wt% Rb), bartonite (0.5 wt% Rb and 2.7–2.9 wt% S), naumannite (Ag$_2$Se), cadmoselitite (Cd$_2$Se), a potentially new mineral of (Na,K,Ba)-Zn sulfide ((Na,K,Ba)$_2$Zn$_2$S$_3$), Ni selenides, and sulfoselenides, as well as slightly hydrated complex Ca-Fe-Cu-S-Se-O compounds (probably oxysulfides and oxyxelenides). The morphology, phase relations, and distributions of elements in coexisting minerals are illustrated in Tables 6 and 7 and in elemental maps (Figures 7 and 8), but many fine phases can hardly be identified as mineral species because they are intimately intergrown.

Akin to the majority of CM rocks in the Tulul al Hammam area [14,18,19], sphalerite marbles contain a set of trace elements (Cd, Ce, Cu, Ni, Th, U, Zn, Zr, Sn) accumulated in simple or double oxide accessories (commonly <10 µm, up to 20–60 µm). These accessories include periclase (with 22–23.5 wt% ZnO, 5.0–6.3 wt% NiO, and 2.5–3.4 wt% CuO), intermediate members of the (Ca,Cd)O solid solutions (0.3–0.9 wt% ZnO), tululite (23.7 wt% ZnO on average), cassiterite, cerianite (Ce,Th)O$_2$, vorlanite (CaUO$_4$), and lakargiite (CaZrO$_3$). Other accessory minerals are scanty lime (CaO), oldhamite (CaS), srebrodolskite, and Fe-Zn spinel (Table 8). Zincite was found only in sample DT-20 with the highest Zn contents, where it is restricted to sulfide-free layers.
Figure 7. BSE image and elemental maps (Zn, S, K, Ba, Fe, Cd, Ni, Cu) showing intimately intergrown sphalerite and Na(K,Ba)-Zn sulfide. Sample DT-26. Ap = fluorapatite, Cal = calcite, Na-Zn-S = Na(K,Ba)-Zn sulfide, Sp = sphalerite. The Na map is not shown here due to Zn-Na overlapping.

Figure 8. BSE image and elemental maps (S, Se, Zn, Cu, Ni, Fe, Ca, O) showing sphalerite coexisting with complex Fe-Ca-Cu-S-O-Se-bearing compounds. Sample DT-25. Ap = fluorapatite, Cal = calcite, Nmn = naumannite, Oxysulf = complex Ca-Fe-Cu-S-Se-O compounds (oxychalcogenides?), Sp = sphalerite, Spu = spurrite.
Table 6. BSE images and EDS compositions (wt%) of sphalerite and associated opaque minerals from the representative CM marble samples.

| BSE Image | Chemical Composition (wt%) | Sample DT-25 | Sample DT-26 | Sample DT-25 |
|-----------|-----------------------------|--------------|--------------|--------------|
|           |                             | Point Zn  Cd  Fe  Mn  Ni  Cu  Ba  Na  K  Ca  S  Se  O  Total | Point Zn  Cd  Fe  Mn  Ni  Cu  Ba  Na  K  Ca  S  Se  O  Total | Point Zn  Cd  Fe  Mn  Ni  Cu  Ba  Na  K  Ca  S  Se  O  Total |
|           |                             | 1  63.47  1.65  0.17  0.15  bdl  bdl  bdl  bdl  bdl  32.08  1.69  bdl  bdl  99.21 | 1  60.78  1.88  1.76  0.19  0.23  bdl  bdl  bdl  bdl  bdl  32.85  1.24  bdl  bdl  98.93 | 1  58.90  1.33  0.50  0.15  1.68  1.77  bdl  bdl  bdl  bdl  31.34  2.71  bdl  bdl  100.25 |
|           |                             | 2  51.89  2.06  0.29  0.24  bdl  4.13  5.36  1.75  bdl  31.23  2.55  bdl  bdl  99.50 | 2  49.99  1.83  3.44  0.27  0.16  bdl  2.18  5.95  1.4  bdl  32.74  1.61  bdl  bdl  99.53 | 2  26.87  1.68  bdl  bdl  21.48  1.96  bdl  bdl  0.24  1.43  27.05  18.29  bdl  bdl  99.00 |
|           |                             | 3  bdl  bdl  14.48  bdl  bdl  23.85  bdl  bdl  0.21  12.46  18.27  7.91  18.2  95.38 | | |
|           |                             | 4  0.62  bdl  1.03  bdl  47.12  1.55  bdl  bdl  0.23  bdl  22.05  26.54  bdl  bdl  99.14 | | |

bdl = below detection limit. * phase mixture. Cal = calcite, Na-Zn-S = Na(K,Ba)-Zn sulfide, Ni-S-Se = Ni sulfo-selenide, Oxysulf = complex Ca-Fe-Cu-S-Se-O compounds (probably oxysulfides), Sp = sphalerite, Spu = spurrite.
Table 7. BSE images and EDS compositions (wt%) of Zn-, Cd-sulfides, and Ag-, Cd-selenides from the sample DT-25.

| BSE Image          | Point | Zn  | Cd | Fe | Ni | Cu | Ag | S   | Se | Total |
|--------------------|-------|-----|----|----|----|----|----|-----|----|-------|
| ![Image 1]         | 1*    | 51.32 | 1.01 | 1.96 | 0.65 | 2.61 | 5.74 | 30.02 | 5.52 | 98.83 |
| ![Image 2]         | 2*    | 8.86  | bdl | 0.97 | bdl | bdl | 61.55 | 7.74  | 20.84 | 99.96 |
| ![Image 3]         | 1     | 56.63 | 1.01 | 1.78 | 0.47 | 3.63 | 31.19 | 3.52  | 99.36 |
| ![Image 4]         | 2     | 1.79  | bdl | bdl | bdl | bdl | 71.48 | 0.54  | 25.79 | 99.60 |
| ![Image 5]         | 1     | 1.47  | 51.5 | 2.06 | 0.67 | 2.71 | bdl  | 8.04  | 32.58 | 99.03 |
| ![Image 6]         | 2     | 1.52  | bdl | 0.48 | bdl | bdl | 70.49 | 0.58  | 25.78 | 99.41 |
| ![Image 7]         | 1     | 4.50  | 69.19 | bdl | bdl | bdl | bdl  | 18.68 | 7.52  | 99.89 |

bdl = below detection limit. * phase mixture. Brm = brownmillerite, Cal = calcite, CaS = oldhamite, CdSe = cadmoselite, CdS = greenockite, Nmn = naumannite, Oxysulf = complex Ca-Fe-Cu-S-Se-O compound (probably oxysulfide), Sp = sphalerite, Spu = spurrite.
The DT marbles are fresh and contain intact spurrite and brownmillerite, sporadic Ca silicate hydrates (CSHs), trace amounts of flourmayenite partially converted into chlormayenite (Ca$_{12}$Al$_{14}$O$_{32}$[□$_{4}$Cl$_{2}$]), as well as lime and oldhamite, which survived although being prone to hydration. The TH marble samples contain CSHs, gypsum, portlandite, U micas, and hydrated Si-bearing Ca$_{2}$U(VI)$_{3}$O$_{10}$ compounds after primary anhydrous Ca-U(VI) oxides, chromatite (CaCrO$_4$), volkonskoite, and other secondary minerals (Table 4) $^{[14,18,19,23]}$.

4.3. Combustion Metamorphic Sphalerite: Abundance, Distribution, and Chemistry

Sphalerite from the Tulul al Hammam CM marbles occurs as compact clusters of abundant coarse grains in DT samples with 1090–1660 ppm Zn and 39–52.7 ppm Cd (Zn/Cd = 27.1–36.9). In TH samples with 231 to 470 ppm Zn and 3 to 75 ppm Cd (Zn/Cd = 4.4–77), only sporadic fine grains of Zn and Cd sulfides were found. The main impurities in the CM sphalerite (Cd, Se, and Fe) reach wt% levels (Table 9). The sphalerite grains are free from compositional zoning (Figures 7 and 9), and thus are advantageous for LA-ICPMS analyses.

Table 8. BSE images and EDS composition (wt%) of oxide accessories associated with sphalerite in the representative CM marble samples.

| BSE Image | Chemical Composition (wt%) |
|-----------|---------------------------|
|           | Sample DT-25              |
|           | Point SiO$_2$ TiO$_2$ Cr$_2$O$_3$ Al$_2$O$_3$ FeO$_3$ MgO CaO ZnO Total |
|           | 1 0.32 0.83 1.86 9.86 42.01 0.23 43.73 0.46 99.30 |
|           | 2 0.41 0.57 1.04 5.78 49.12 0.38 42.52 0.36 100.18 |
|           | Sample TH-52              |
|           | Point SiO$_2$ TiO$_2$ Cr$_2$O$_3$ Al$_2$O$_3$ FeO$_3$ MgO CaO ZnO Total |
|           | 1 bdl 0.60 0.47 5.21 75.03 5.49 bdl 13.09 99.89 |
|           | Sample DT-25              |
|           | Point SiO$_2$ CaO MgO UO$_3$ Total |
|           | 1 0.85 16.25 0.80 81.50 99.40 |

bdl = below detection limit. Ap = fluorapatite, Brc = brucite, Brm = brownmillerite, Cal = calcite, CSHs = calcium silicate hydrates, Spl = spinel-group mineral, Srb = srebrodolskite, Vrl = vorlanite.
Table 9. Selected typical compositions of sphalerite from CM marbles, Tulul al Hammam area (EDS and EPMA data, wt%).

| Sample | DT-20 | DT-25 | DT-26 | TH-11 | TH-74 |
|--------|-------|-------|-------|-------|-------|
|        | 1     | 2     | 3     | 4     | 5     | 6     | 7     | 8     | 9     | 10    | 11    | 12    | 13    |
| Zn     | 63.14 | 63.99 | 63.97 | 64.11 | 60.23 | 64.76 | 59.80 | 61.43 | 63.02 | 61.27 | 65.21 | 64.81 | 53.71 |
| Cd     | 1.93  | 1.93  | 2.03  | 1.91  | 1.32  | 1.67  | 3.14  | 1.15  | 1.70  | 3.53  | 1.07  | 1.55  | 14.07 |
| Fe     | 0.16  | 1.41  | 1.39  | 1.32  | 0.85  | 0.17  | 1.15  | 3.48  | 1.78  | 2.03  | 0.40  | 0.44  | 1.56  |
| Mn     | 0.11  | 0.10  | 0.10  | 0.10  | <0.10 | <0.10 | <0.10 | <0.10 | 0.23  | 0.19  | 0.17  | 0.19  | <0.10 | 0.56  |
| Ni *   | <0.10 | <0.10 | <0.10 | <0.10 | 1.11  | <0.10 | 0.35  | <0.10 | 0.23  | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 |
| Cu *   | <0.15 | <0.15 | <0.15 | <0.15 | 0.93  | <0.15 | 1.04  | <0.15 | <0.15 | <0.15 | <0.15 | <0.15 | <0.15 | <0.15 |
| S      | 31.91 | 32.78 | 32.52 | 31.38 | 29.53 | 32.38 | 29.50 | 32.50 | 32.44 | 32.28 | 32.30 | 32.07 | 30.03 |
| Se     | 0.75  | 0.32  | 0.30  | 0.57  | 5.10  | 1.71  | 4.54  | 1.37  | 1.05  | 0.87  | 0.96  | 1.29  | 0.47  |
| Total  | 99.01 | 100.43| 100.20| 99.29 | 99.07 | 100.69| 99.53 | 100.16| 100.43| 100.14| 100.12| 100.16| 100.40|
|        |       |       |       |       |       |       |       |       |       |       |       |       |       |

Formula based on $\Sigma S + Se = 1$

$\Sigma M = Zn + Cd + Fe + Mn + Ni + Cu.$

Figure 9. BSE image and elemental maps (S, Zn, Fe, Cu, Ni) showing the chemical homogeneity of sphalerite from sample DT-25. Ap = fluorapatite, Cal = calcite, Oxysulf = complex Ca-Fe-Cu-S-Se-O compounds (oxychalcogenides ?), Sp = sphalerite.

Cadmium in CM sphalerite is 2.01 wt% on average ($X_{av}$ over N = 200 determinations) (Figure 10; Table 10). At least 1 wt% Cd is present at every analyzed point, but it rarely exceeds 3 wt%. The Cd contents are the highest (14.0 wt%) in the smallest sphalerite grains from sample TH-74 with the lowest Zn/Cd ratio of 4.4. Cd-rich sphalerites from samples TH-74 and DT-25 coexist with sporadic tiny grains of primary or secondary greenockite (Cd$_{0.73-0.99}$Zn$_{0.19-0.35}$Fe$_{0.02-0.07}$S$_{0.80-0.98}$Se$_{0.02-0.20}$) and very rarely with cadmoselite (CdSe) (Tables 7 and 11). The Cd concentrations in CM sphalerites poorly correlate with the contents of other elements.
Selenium is another ubiquitous impurity in the CM sphalerites. It is uniformly distributed within each grain (Figure 8) but varies mostly from 0.3–0.8 wt% to 1.4 wt% between grains even in the same thin sections (Tables 9 and 10; Figure 10). The average Se contents are in a range of 0.51–1.12 wt%. Expectedly, the highest Se concentration ($X_{av} = 4.27$ wt%; $X_{max} = 6.68$ wt% Se) was obtained for sample DT-25 with 503 ppm of bulk Se. Se-rich sphalerite belongs to assemblages that include Se-rich Ni, Cu, and Ag sulfides, selenides, and oxysulfides (Tables 4 and 7; Figure 8). However, in the same sample Se in coarse sphalerite grains outside selenide accumulations ranges from 1.7 to 4.3 wt% Se. The Se content is the highest (up to 10.61 wt%; $X_{av} = 5.78$ wt%) in greenockite and cadmoselite ((Cd,Zn)(Se,S)).

Iron is in a range of 1.2–2.2 wt% ($X_{av} = 1.46$ wt%; $N = 185$) in most of the analyzed sphalerite grains (Tables 9 and 10; Figure 10). It is the lowest (0.31–0.64 wt%) in sphalerite from sample TH-11 and the highest in that from DT-26 (up to 3.74 wt%).

Consistent SEM-EDS, EPMA, and LA-ICPMS data for the representative sample DT-20 (Tables 3, 9 and 10), as well as elemental mapping (Figures 7 and 9), confirm the uniform distribution of Cd, Se, and Fe in the CM sphalerites. Single-crystal XRD data (see below) prove that these elements are randomly distributed in the cubic ZnS structure.

Manganese in the analyzed sphalerites is most often below the EDS-SEM detection limit (< 0.1 wt%). Sporadic spikes of 0.18–0.66 wt% Mn may be due to inclusions of secondary Mn (oxy)hydroxides. LA-ICPMS measurements reveal ~1440–1780 ppm Mn ($X_{av} = 1565$ ppm; $N = 16$) in sphalerite from DT-20 and as low as 355 ppm in DT-25. Generally, the contents of Mn are an order of magnitude higher than those of cobalt and nickel. Co contents reach 172 ppm ($X_{av} = 124$ ppm in DT-20 and $X_{av} = 66$ ppm in DT-25) (Table 3). The average Ni contents in large homogeneous sphalerite crystals are 265 ppm in DT-25) (Table 3). The average Ni contents in large homogeneous sphalerite crystals are 265 ppm in DT-25.

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Table 10. Average compositions of sphalerite from CM marbles, Tulul al Hammam area (SEM-EDS and EPMA, wt%).

| Sample   | DT-20 (n = 45) | DT-25 (n = 21) | DT-26 (n = 53) | TH-11 (n = 10) |
|----------|----------------|----------------|----------------|---------------|
|          | Mean | S | Min | Max | Mean | S | Min | Max | Mean | S | Min | Max | Mean | S | Min | Max |
| Zn       | 63.28 | 0.43 | 62.44 | 63.99 | 61.16 | 1.86 | 58.46 | 64.96 | 61.98 | 0.84 | 60.54 | 64.19 | 64.80 | 0.34 | 64.07 | 65.24 |
| Cd       | 2.02  | 0.28 | 1.63  | 2.64  | 1.84  | 0.95 | 1.34  | 2.21  | 1.06  | 0.14 | 1.04 | 3.73 | 3.15 | 0.17 | 1.07 | 1.55 |
| Fe       | 1.28  | 0.11 | 1.04  | 1.44  | 1.13  | 0.60 | <0.10 | 2.15  | 2.22  | 0.54 | 1.55 | 3.71 | 0.45 | 0.09 | 0.32 | 0.66 |
| Mn       | 0.10  | 0.06 | <0.10 | 0.16  | <0.10 | <0.10 | <0.10 | 0.15  | 0.07 | <0.10 | 0.24 | <0.10 | –   | <0.10 | <0.10 |
| Ni *     | <0.10 | –   | <0.10 | 0.30  | 0.46  | 0.47 | <0.10 | 1.83  | <0.10 | <0.10 | 0.31 | <0.10 | –   | <0.10 | <0.10 |
| Cu *     | <0.15 | –   | <0.15 | 0.85  | 0.69  | <0.15 | 2.70  | <0.15 | –   | <0.15 | <0.15 | –   | <0.15 | <0.15 | <0.15 |
| S        | 32.56 | 0.33 | 31.91 | 33.10 | 30.10 | 27.86 | 32.47 | 32.45 | 0.25 | 31.83 | 32.99 | 32.15 | 0.19 | 31.78 | 32.41 |
| Se       | 0.51  | 0.13 | 0.29  | 0.75  | 4.27  | 1.67 | 1.39  | 6.68  | 1.12 | 0.13 | 0.77 | 1.37 | 1.05 | 0.14 | 0.87 | 1.29 |
| Total    | 99.65 | 99.81 | 100.13 | 100.13 | 100.13 | 100.13 | 100.13 | 100.13 | 100.13 | 100.13 | 100.13 | 100.13 | 100.13 | 100.13 | 100.13 |

Concentrations of Co (<0.10 wt%) and Ag (<0.15 wt%) are below detection limit. * may be captured from coexisting phases during analysis. n = number of analyses, Mean = mean value, S = standard deviation, Min = minimum value, Max = maximum value.

Table 11. Representative analyses and average composition of greenockite from CM marbles, Tulul al Hammam area (SEM-EDS, wt%).

| Sample | TH-74 | DT-25 |
|--------|-------|-------|
|        | 1     | 2     | 3     | 4     | 5     | 6     | 7     | DT-25 (n = 14) |
| Cd     | 55.74 | 79.04 | 69.94 | 69.97 | 64.54 | 63.46 | 63.07 | 68.29 | 4.79 | 63.07 | 75.05 |
| Zn     | 17.93 | 18.60 | 18.78 | 18.64 | 17.31 | 22.03 | 21.62 | 19.46 | 1.38 | 17.31 | 22.03 |
| S      | 24.21 | 5.32  | 6.45  | 7.39  | 10.61 | 2.71  | 3.11  | 5.78  | 2.07 | 2.71  | 10.61 |
| Se     | 1.37  | 99.25 | 99.06 | 99.94 | 100.65 | 99.03 | 99.04 | 99.49 |       |       |       |
| Total  | 100.00| 99.25 | 99.94 | 100.65 | 99.03 | 99.04 |       |       |       |       |       |

Formula based on one S atom

Cd 0.642 1.031 0.932 0.917 0.852 0.783 0.786 0.893
Zn 0.355 0.016 0.089 0.098 0.186 0.230 0.241 0.134
S 0.978 0.896 0.878 0.861 0.801 0.952 0.945 0.892
Se 0.022 0.104 0.122 0.139 0.199 0.048 0.055 0.108
ΣCd+Zn 0.997 1.047 1.021 1.015 1.037 1.012 1.027 1.028

Mn, Fe, Ni (<0.10 wt%), Cu (<0.15 wt%) are below detection limit. n = number of analyses, Mean = mean value, S = standard deviation, Min = minimum value, Max = maximum value.
The composition of smaller sphalerite grains that coexist with intricately intergrown Ni, Cu, and Ag sulfides and selenides was resolvable only by SEM-EDS. Such grains commonly contain 0.3–3.0 wt% Ni and 0.4–2.7 wt% Cu. A few grains with naumannite (Ag$_2$Se) inclusions also bear 1.3–3.0 wt% Ag. The element contents are unevenly distributed and have a high standard deviation commensurate with average concentrations, possibly, because of submicrometer inclusions of the respective phases irresolvable even in BSE images (Tables 7 and 9).

Mercury concentrations in the CM sphalerites (Table 3) are relatively high (132 and 226 ppm), being of the same order of magnitude as in the authigenic ZnS precursors (345 ppm). Copper varies from 3.7 to 33.4 ppm ($X_{av} = 11.1$ ppm).

The contents of other elements revealed by LA-ICPMS in different crystals of the representative marble sample DT-20 are 0.3–1.37 ppm Ga ($X_{av} = 0.45$ ppm), 0.15–0.62 ppm Ag ($X_{av} = 0.42$ ppm), 4.11–4.9 2 ppm In ($X_{av} = 4.51$ ppm), 0.83–1.53 ppm Sn ($X_{av} = 1.10$ ppm), and 0.18–6.33 ppm Sb ($X_{av} = 1.19$ ppm) (Table 3). The Cu, Ag, Sn, and Sb concentrations in a few large sphalerites from sample DT-25 with higher TE loading are within the same ranges, while In and Ga are slightly higher (2.44 and 7.9 ppm, respectively). Sphalerites from both samples are depleted in Ge, As, Mo, Te, Ti, Bi, Pb, Au, and Pt, which are below the detection limits. SEM-EDS and EPMA data for accessories in the Jordanian CM marbles revealed Cd and Se enrichment and the presence of Fe in sphalerites. Other important impurities have never been reliably detected by EPMA as lattice-bound species. Spikes of Cu, Ni, and/or Ag are most likely associated with submicron inclusions. On the other hand, analysis of sphalerite has systematically shown deficient totals (up to 1 wt%), especially in high-quality homogeneous sphalerite crystals from DT-20 free from micrometer inclusions (Figure 5C–F). We tentatively attribute the deficit to some impurities that may have concentrations below the EPMA detection limits. However, the exhaustive trace-element determinations by LA-ICPMS (Table 3) fail to account for the whole difference: The TE total (without Cd, Se and Fe) is no higher than 0.2 wt%. Otherwise, the deficit of totals may be due to the oxygen detected in some crystals by SEM-EDS in amounts of 0.5–1.0 wt%, but these results can only be used as diagnostic because of a high detection limit (0.4 wt%) and a very large relative error (40% at low contents). The S$^{2-}$ → O$^{2-}$ substitution range was constrained by single-crystal XRD.

4.4. X-Ray Diffraction and Crystal Structure

Crystal structure was determined in a pure transparent sphalerite crystal (~160 × 80 × 60 μm), with a 0.65 wt% deficit of totals, which was extracted from sample DT-20 (Table 9, analysis 4). The mineral is cubic ZnS, with cell parameters of $a = 5.40852(12)$ Å, $V = 158.211(6)$ Å$^3$, and $Z = 4$. Systematic absence of reflections is consistent with the space-group $\text{I}4\text{m}$. The unit-cell size of (Zn,Cd,Fe)(S,Se,O) approaches that of pure ZnS ($a = 5.4094$ Å [56]). The crystal structure was solved and refined on the basis of $\text{F}^2$ using the SHELX software (Version 2018/3, Göttingen University, Göttingen, Germany) [57]. Like the pure endmember ZnS$_{\text{cub}}$, natural sphalerite has a zinc blende-type structure, without any discernible ordering of cations and/or anions and/or superstructure. Single-crystal XRD failed to reveal any reflections that would represent inclusions or domains of extraneous (e.g., O-bearing) phases, such as ZnO or Zn sulfates.

The structure (Table 12) was refined assuming Zn$^{2+}$, Cd$^{2+}$, and Fe$^{2+}$ M-site occupancy proceeding from chemical analyses. The share of Se in the anionic occupancy was inferred from EPMA and SEM-EDS data. The S and O occupancies of the anionic position were refined assuming its full population.

The resulting formula of the sphalerite is $\text{Zn}_{0.96}\text{Cd}_{0.02}\text{Fe}_{0.02}(\text{S}_{0.946(6)}\text{Se}_{0.046(6)}\text{O}_{0.007(4)})\Sigma 1.00$. The XRD analysis detected an excess of oxygen atoms relative to the composition determined by chemical analyses (given that oxygen was assumed to account for the deficit of totals) and the corresponding deficit of sulfur, but the difference is about the error in the respective element contents.

The analyzed sphalerite has a smaller unit-cell size ($a$ parameter) than pure ZnS$_{\text{cub}}$. As Skinner and Barton (1960) [58] found out, the $a$ parameter decreases as oxygen substitutes for sulfur: to 5.4081 Å at 0.4 mol% ZnO and to 5.4065–5.4070 Å at 0.8 mol% ZnO. The sample we analyzed, with ~0.5 mol%
ZnO, has only a slightly greater unit cell of 5.40852(12) Å, due to the complex composition of the natural crystal. The presence of Cd, Fe, and Se impurities in the structure jointly leads to a minor unit cell increase. Among all impurities present in the sample, Cd causes the strongest influence on the cell size while the effect of Fe is less significant [59–61].

The valence of cations for ((Zn,Cd,Fe))(S,O,Se) calculated using the bond valence sum (BVS) formula is +2.04 and approaches that for pure sphalerite (+2.02), with the $v_{ij} = \exp[(R_{ij} - d_{ij})/0.37]$ contribution of each bond with the distance $d_{ij}$ to the valence, where $R_{ij}$ as an empirical parameter and the total valence $V_j$ of the atom $i$ is $V_j = \sum v_{ij}$ [62].

Thus, the natural crystal of the complex composition ((Zn,Cd,Fe))(S,O,Se) is isostructural to sphalerite and has a disordered distribution of all elements according to the respective $ZnS_{\text{cub}}$ positions.

Table 12. Crystal parameters, data collection and structure refinement details for Fe-, Cd-, Se-, O-bearing sphalerite.

| Chemical Formula | $Zn_{0.96 \pm 0.02}Cd_{0.02}Fe_{0.02}(S_{0.946(8)}O_{0.046(8)}Se_{0.0074})_{\gamma=1.00}$ |
|------------------|-----------------------------------------------------------------|
| Space group      | $F43m$                                                           |
| $a$ (Å)          | 5.40852(12)                                                      |
| $V$ (Å$^3$)      | 158.211(6)                                                       |
| $Z$              | 4                                                                |
| Crystal size (mm)| $0.16 \times 0.08 \times 0.06$                                 |
| $d$ (g/cm$^3$)   | 4.110                                                           |
| F(000)           | 184                                                              |
| $\mu$ (MoKα) (mm$^{-1}$) | 16.115                                                          |
| $\theta$ range for data collection | 6.535 to 31.711                                                  |
| Index ranges     | $-7 \leq h \leq 7; -7 \leq k \leq 7; -7 \leq l \leq 8$          |
| Scan width (°/frame) | 1                                                               |
| Exposure (s/frame)| 30                                                              |
| No. of measured reflections | 770                                                             |
| No. of unique reflections | 43                                                              |
| No. of observed reflections ($I > 2\sigma(I)$) | 43                                                              |
| No. of parameters refined | 6                                                               |
| $R_{int}$        | 0.0271                                                           |
| Extinction coefficient | 0.0060(11)                                                      |
| Flack parameter  | -0.002(17)                                                       |
| $R1$, $wR2$ for $I > 2\sigma(I)$ | 0.0075, 0.0176                                                  |
| $R1$, $wR2$ all data | 0.0075, 0.0176                                                  |
| GooF             | 1.106                                                            |
| Residual electron density ($e/Å^3$) | 0.274-0.249                                                    |

| Atom coordinates, $U_{eq}$ (Å$^2$) values, and occupancies |
|-----------------------------------------------------------|
| M | $x$ | 0.25 |
|   | $y$ | 0.25 |
|   | $z$ | 0.25 |
|   | Occupancy |
|   | $Zn_{0.96 \pm 0.02}Cd_{0.02}Fe_{0.02}$ | 0.01145(11) |
| S,Se,O | $x$ | 0 |
|       | $y$ | 0 |
|       | $z$ | 0 |
|       | Occupancy |
|       | $S_{0.946(8)}Se_{0.0074}O_{0.046(8)}$ | 0.00833(3) |

4.5. Raman Spectroscopy

4.5.1. First-Order Raman Spectrum

The recorded Raman spectra of the Tulul Al Hamman CM sphalerites are generally similar to those reported in the literature, including the RRUFF database (an integrated database of Raman spectra, X-ray diffraction and chemistry data for minerals) [63,64] (Figure 11). Factor-group analysis of vibration modes of the cubic $F43m$ ($T_d^2$) cell of $ZnS_{\text{cub}}$ (zinc blende-type of structure) predicts two (acoustic and optical) triple-degenerated modes, which both have the same symmetry $F_2$ at
the central point $\Gamma$ of the Brillouin zone. Namely, the $F43m$ structure at the ambient conditions has total irreducible representation at $k = 0$: $\Gamma = 2F_2$. According to our LADY (LAttice Dynamics) calculations of lattice dynamics, only one triple-degenerated optical mode $F_2$ is active in the first-order Raman spectrum: the one that represents the stretching vibrations of the (Zn,Fe,Cd)-S bond in corner-connected tetrahedra $(\text{Zn,Fe,Cd})_4S_4$. This mode splits into double-degenerated transverse (TO) and longitudinal (LO) components upon the interaction of electron states and atomic vibrations with the electromagnetic field of photons.

The first-order Raman spectrum of sphalerite (Figure 12) exhibits one very strong LO band at 344 cm$^{-1}$ and one weak TO band at 276 cm$^{-1}$, which agree with the lattice dynamics modeling. However, it additionally contains two very strong bands at 299 and 331 cm$^{-1}$, as well as a satellite band of moderate intensity at 309 cm$^{-1}$ with a shoulder of the 299 cm$^{-1}$ band. All these bands are interpreted in Table 13.

![Figure 11](image_url)

**Figure 11.** Raman spectra of natural CM sphalerite from sample DT-20 (1) compared with sphalerite from Arizona [RRUFF base] (2).

The spatial micro-Raman analysis of the sample applied to many points of sphalerite grains proves the homogeneity of the solid solution. It revealed no inclusions of extraneous phases (oxides, sulfates, sulfites etc.), layers or films of Zn oxide, or other O- and Zn-bearing compounds, e.g., no bands at 437 and 524 cm$^{-1}$ (the latter with a shoulder at 562 cm$^{-1}$) corresponding to hexagonal zincite ZnO.

4.5.2. Second-Order Raman Spectrum

The second-order Raman spectrum is more intense than the first-order one and more intense than the spectrum of crystalline Si. It contains peaks that represent the density of phonon states at critical points of the Brillouin zone. The bands observed in the spectrum are assigned to combinations of the critical points in cubic ZnS (Table 14). The obtained Raman spectrum of CM sphalerite is similar to that of synthetic sphalerite reported by [63], with similar or the same frequencies (Table 14).
4.5.3. Resonant Raman Scattering

Raman spectra collected at excitation wavelengths of 325 (green line, a) and 325 nm (UV line, b) show resonance at UV excitation, with overtones of the basic tone (LO mode 348 cm\(^{-1}\)) (Figure 12; Table 13). The wavenumber of strong bands (nLO) in the resonant spectra of the analyzed sphalerite depends linearly on the number n of repeated basic tone reflections, which appears in the spectra of the (Zn,Cd,Fe)(S,O,Se)\(_{\text{cub}}\) crystal (Figure 13).

![Raman spectra](image)

**Figure 12.** Raman spectra of the Tulul al Hammam CM sphalerite at 532 (A) and 325 nm (B) excitation. See resonant light scattering in the UV excitation pattern, with several overtones (Table 13) of the main tone (LO mode 348 cm\(^{-1}\)). The spectra of record a calcite microinclusion (band 1086 cm\(^{-1}\)) in panels (A) and air N2 (sharp band at 2331 cm\(^{-1}\)) in (B).

**Table 13.** Features of first-order Raman spectra of natural CM sphalerite and their interpretation.

| This Study \(\lambda_L = 532 \text{ nm} \) \(\nu(cm^{-1})\) | This Study \(\lambda_L = 325 \text{ nm} \) \(\nu(cm^{-1})\) | Data from [63] \(\lambda_L = 514 \text{ nm} \) \(\nu(cm^{-1})\) | Data from [64] \(\lambda_L = 514 \text{ nm} \) \(\nu(cm^{-1})\) | Data from [64] \(\lambda_L = 325 \text{ nm} \) \(\nu(cm^{-1})\) | Interpretation of Bands |
|---|---|---|---|---|---|
| 276 | 275 | 275 | 277 | 277 | TO |
| 299 | 298 | | | | LO(X1) |
| 309 | 309 | | | | LO(X2) |
| 331 | 331 | | | | LO(X3) |
| 349 | 348 | 350 | 348 | 348 | LO |
| 276 | 275 | 275 | 277 | 277 | TO |
| 299 | 298 | | | | LO(X1) |
| 309 | 309 | | | | LO(X2) |
| 331 | 331 | | | | LO(X3) |
| 349 | 348 | 350 | 348 | 348 | LO |
| 696 | | | | | 2LO |
| 1042 | | | | | 3LO |
| 1394 | | | | | 4LO |
| 1737 | | | | | 5LO |

Natural sphalerite (this study): sample DT-20.
Table 14. Features of second-order Raman spectra of ZnScub (sphalerite) and their interpretation.

| This Study $\nu$(cm$^{-1}$) | Data from [63] $\nu$(cm$^{-1}$) | Interpretation of Bands |
|-----------------------------|-------------------------------|-------------------------|
| 147                         | 142                           | 2TA$_L$                 |
| 180                         | 180                           | 2TA$_X$                 |
| 198                         | (TO − TA$_u$)$_\Sigma$        |
| 218                         | 219                           | (TO − TA)$_X$          |
| 234                         | 239                           | 2TA$_\Sigma$           |
| 304                         | (LA + TA)$_W$                 |
| 309                         | 312                           | (LA + TA$_u$)$_W, \Sigma$|
| 336                         | Not assigned                  |
| 346                         | Not assigned                  |
| 385                         | 380                           | 2LA$_\Sigma$           |
| 399                         | 397                           | (TO + TA)$_X$          |
| 420                         | 420                           | (LO + TA)$_X$          |
| 447                         | 450                           | (LO + TA)$_L$          |
| 483                         | (TO$_l$ + LA)$_\Sigma$        |
| 515                         | 517                           | (LO + LA)$_\Sigma$     |
| 607                         | 615                           | 2TO$_W$                |
| 612                         | 615                           | 2TO$_X$                |
| 637                         | 638                           | (LO + TO)$_L$          |
| 668                         | 668                           | 2LO$_X$                |
| 685                         | 693                           | 2LO$_L$                |
| 700                         | 700                           | 2LO$_\Gamma$           |

Raman spectra of this study for natural sphalerite are compared with published data for synthetic sphalerite [63]. Natural sphalerite (this study): sample DT-20.

Figure 13. Wavenumber of strong bands ($n$LO) in resonant Raman spectra of CM sphalerite, at 325-nm excitation, as a function of the number $n$ of repeated basic tone reflections (LO mode 348 cm$^{-1}$).
5. Discussion

5.1. Fractionation of Metals (Fe, Mn, Cd, Hg, In, Ga) and Chalcogenides (Se, Te, As, Sb) in ZnS: a Brief Overview

Sphalerite (cubic) and würtzite (hexagonal) ZnS polymorphs have only a minor enthalpy difference (from 2 to 13 kJ mol\(^{-1}\)) at ambient conditions. This small difference alone cannot account for greater stability of the zinc blende structural type and its wide spread in both natural and synthetic ZnS systems, given that the würtzite type is more stable in the case of CdS [65]. In the latter publication, the stability of the two structure types was explained proceeding from the respective interatomic potentials of ZnS and CdS and from their ability to reproduce many properties of sphalerite, würtzite, greenockite, and hawleyite (CdS\(_{\text{cub}}\)). The same approach can be useful to understand the fractionation of Zn, Cd, and some other TE in natural sulfidic assemblages containing ZnS and/or CdS.

The sphalerite structure can accommodate many ions comparable in size with tetrahedrally coordinated Zn\(^{2+}\) and has an affinity to tetrahedral coordination due to sp\(^3\) hybrid orbitals [65,66]. This hybridization type is typical of Cd\(^{2+}\), Hg\(^{2+}\), Ga\(^{3+}\), In\(^{3+}\), and Ag\(^+\), and, possibly, also of Cu\(^{+}\), Ti\(^{3+}\), Ge\(^{4+}\), and Sn\(^{4+}\). Unlike the isovalent substitutions Zn\(^{2+}\) → Me\(^{2+}\) (Me = Cd, Fe, Mn, and Hg), other cations like In\(^{3+}\), Ga\(^{3+}\), and Ag\(^+\) incorporate into ZnS\(_{\text{sp}}\) through heterovalent schemes. The isovalent substitutions produce diverse multicomponent solid solutions, namely FeS, CdS, HgS, and ZnSe, that have a cubic zinc blende-type structure: rudashevskyite (FeS\(_{\text{cub}}\)), hawleyite (CdS\(_{\text{cub}}\)), metacinnabar (HgS\(_{\text{cub}}\)), and stilleite (ZnSe\(_{\text{cub}}\)) [1,67–69]. Alabandite (MnS\(_{\text{cub}}\)) belongs to the galena structural type, and the (Zn,Mn)S\(_{\text{cub}}\) solid solutions are more restricted than (Zn,Fe)S\(_{\text{cub}}\). The (Zn,Fe,Mn)S\(_{\text{cub}}\) homogeneous solid solutions may contain up to ~4 wt% (7 mol%) Mn. Rambertite (MnS\(_{\text{hex}}\)) has the würtzite-type structure, and (Zn,Mn)S\(_{\text{sp}}\) crystals adopt this structure type or contain separate domains of sphalerite and würtzite, where the share of MnS endmember in (Zn,Mn)S\(_{\text{sp}}\) solid solution can reach 50 mol% [70]. Therefore, natural sphalerites commonly contain a few wt% of Fe or Mn, and smaller amounts of Cd, Hg, and/or Se. The three latter elements, being common impurities, rarely reach high contents in natural sphalerites. Such ‘anomalous’ sphalerites are restricted to particular environments. Chemically pure ZnS sphalerite or würtzite are of scarce natural occurrence.

Iron and manganese can easily incorporate into the sphalerite structure at higher temperatures [61,71]. They reach the highest contents in meteorite sphalerites (25.3–32.1 wt% Fe or 42–50 mol% Fe\(_{\text{cub}}\)) [72] and in ultra-high-temperature contact spurrite-mervinite marbles (19.0–20.7 wt% Fe; 4.0–5.9 wt% Mn; Zn\(_{0.35–0.38}\)Fe\(_{0.32–0.33}\)Mn\(_{0.07–0.10}\)S) [73]. The incorporation of large amounts of Mn stabilizes the würtzite structure [71], and würtzite from the contact marbles contains similar concentrations of Fe and Mn: 12.0 to 19.1 wt% and 16.8 to 18.3 wt%, respectively (Zn\(_{0.39–0.46}\)Fe\(_{0.19–0.31}\)Mn\(_{0.28–0.30}\)S) [73].

The contents of Cd, Hg, and Se in sphalerite are very high only in the geochemical environments where these elements and their ratios (Cd/Zn, Hg/Zn, or Se/S) are high as well. This is the case of active fumaroles at Kudriavy volcano (Iturup Island, Russia) with unique In, Cd, Zn, Cu, Mo, Re, and Bi sulfide mineralogy [74,75] and two types of ZnS-CdS solid solutions: (Zn,Cd,Fe)S\(_{\text{cub}}\) containing up to 8 mol% CdS and (Zn,Cd,Fe)S\(_{\text{hex}}\)-(Cd,Zn,Fe)S\(_{\text{cub}}\) with ~17–100 mol% CdS. Although hawleyite, a cubic CdS, is stable above 525 °C [76], the contents of Cd in ZnS\(_{\text{sp}}\) become much lower at higher temperatures (Figure 14) [74,77]. Nevertheless, restricted solid solutions of (Zn\(_{1–0.5}\), Cd\(_{0.5} \)S\(_{\text{cub}}\) can be synthesized by chemical transport reactions in the temperature range from 700 to 1100 °C [71]. In natural environments, at higher temperatures, cadmium in Cd-rich growth media becomes ever more prone to form its own phases rather than being a member of solid solutions with Zn counterparts, which is true for both sulfide and oxide compounds [19,65].

Mercury is often stored in sphalerite from complex sulfosalt-HgS deposits, up to the composition (Zn\(_{0.732}\)Hg\(_{0.268}\)S) [78], e.g., Hg content in sphalerite from Eskay Crek, Canada, reaches 16.4 wt% [79]). Some Hg-rich sphalerites also contain up to 7.96 wt% Cd [78].

Selenium reaches thousands of ppm in sphalerite from black shale deposits [80] and 0.12 wt% Se was reported from sphalerite coexisting with other Se-bearing sulfides [81]. Note in this respect that
Se in the Muwaqqar Fm. ‘oil shales’ resides mostly in authigenic pyrite (6535 ppm Se) rather than in authigenic ZnS (282 ppm) (Table 3).

Sphalerites with high indium contents are very rare but are known from high-temperature fumarolic crusts in Kudriavy volcano and from the Toyoha Cu-Zn-In epithermal deposit (Japan), where In reaches 4.75 wt% and 5.9 wt%, respectively [1,74,75]. Both sphalerite and wurtzite from Kudriavy volcano underwent heterovalent substitutions \[2\text{Me}^{2+} \rightarrow \text{Cu}^{+} + \text{In}^{3+}\] (Me = Zn, Cd, Fe). The zinc blende structure has a higher storage capacity than wurtzite relative to In and Cu [74]: up to 2.9 wt% Cu and 4.75 wt% In in sphalerite and 1.3 wt% Cu and 2.8 wt% In in wurtzite, which corresponds to the Cu/In molar ratio of about 1. According to the phase diagram of the \((\text{ZnS})_3x-(\text{In}_2\text{S}_3)_{1-x}\) system, the zinc blende-type structure can accommodate up to 10% of \(\text{In}_2\text{S}_3\) [71].

\[\text{Figure 14.} \] Phase diagram of the system ZnS–CdS; \(x\)—the molar fraction of Cd in \(\text{Zn}_{1-x}\text{Cd}_x\text{S}\) solid solution. Phase boundaries after [77]. Orange (sphalerite and wurtzite) and yellow (greenockite) colors show the composition ranges of sulfides from different rock types: (1) spurrite marbles from Kochumdek contact aureole (Podkamennaya Tunguska Basin, East Siberia), after [73]; (2) CM marbles from Tulul al Hammam area (Daba-Siwaqa complex, Central Jordan), this study; (3) fumarolic mineralization of Kudriavy volcano (Iturup Island, Kuriles), after [74]; (4) immature organic-rich siliceous chalks (‘oil shales’) of the Muwaqqar Chalk Marl Formation, after [14] and this work.

The tetrahedral coordination of \(\text{Ga}^{3+}\) in chalcogenide compounds, with \(sp^3\) hybrid orbitals [66], favors the incorporation of Ga into sphalerite at high temperatures. The amounts of Ga reach ~25 mol% and 16.3 mol% at 900 and 800 °C, respectively, in the Zn-Ga-S system and 27.4 mol% Ga at 800 °C in the Zn-Fe-Ga-S system [82]. At higher contents of Ga, the ZnS-Ga2S3 system develops triple compounds like \(\text{ZnGa}_2\text{S}_4\), \(2\text{ZnS} \cdot 3\text{Ga}_2\text{S}_3\), or \(\text{ZnS} \cdot 3\text{Ga}_2\text{S}_3\) [71]. In spite of the possibility for Ga to incorporate into the zinc blende lattice, natural Ga-rich sphalerites are yet unknown, likely, because Ga is a trace element.
which rarely exceeds upper crust contents in natural ore-forming systems. The highest Ga contents in sphalerite (up to 366 ppm) were reported from epithermal deposits in SE Europe and Japan [1].

Although sphalerite is sometimes considered as a carrier of silver, in practice higher Ag concentrations are almost always related to microscopic or submicroscopic inclusions of discrete Ag minerals [1], which is supported by the eutectic-type phase diagram of the ZnS-Ag2S system. The ultimate solubility of Ag2S in ZnS reaches 0.011%, 0.022%, and 0.052% at 600, 700, and 750°C, respectively, as it was estimated by saturation of solid ZnS with silver [71].

The substitution of Zn2+ by ions with other hybridization types, such as Co2+, Ni2+, Sb3+, Mo4+, Pb2+, or Bi3+, is strongly limited. Namely, Ni incorporated into ZnS is at most 1% NiS in hydrothermally synthesized samples [71]. Incorporation of monovalent (Cu+, Ag+), trivalent (In3+, Ga3+, Fe3+, Ti3+), and tetravalent (Ge4+, Sn4+, Mo4+) elements may be evidence of coupled isomorphic substitutions, such as 2M+ + M2+ + M4+ → 4Zn2+ or even more complex schemes [1]. M3+ and M4+ can enter the sphalerite structure due to the formation of donor-acceptor pairs with monovalent ions [83].

As for anionic species, only Se reaching several wt% has been revealed so far in sphalerite. Confirmations of arsenic-bearing sphalerites in the electron microprobe era have been few [1]. The As concentrations about hundreds of ppm reported for black shale-hosted sphalerite [80] appear to be the highest among natural occurrences known before. According to our data (Table 3), authigenic ZnS modifications from the Muwaqqar Fm. ‘oil shales’ contain 2255 ppm As. Antimony is not a common impurity in sphalerite, with its highest reliable values most likely ranging within 0.24–0.55 wt% Sb, except for sphalerite from the epithermal Au-Te Săcărimb deposit (Romania) where it reaches 500–1000 ppm. The contents of Bi in natural sphalerite are moderate, and tellurium is ≤ 0.05 ppm [1,84]. We know quantitative estimates only for Te solubility in ZnS indicating that incorporation of 5·10−4 wt% Te into the ZnS system produces inclusions of discrete phase in single crystals of ZnS [71].

Compared to sphalerite from main economic deposits, authigenic ZnS modifications from the Muwaqqar Fm. ‘oil shales’ show particular combinations of TE signatures (Table 3; Figure 15). In addition to anomalously high Cd enrichment (~6.6 to 8.1 wt% on average), they contain up to 7760 ppm Cu, 2145 ppm Sb, 645 ppm Ag, ~600 ppm Mo and Pb, and 200 to 345 ppm Ge, Ga, and Hg. At the same time, they are depleted in Se (~280 ppm) and bear only trace amounts of Mn, Ti, In, and Bi, while the contents of Co, Te, and Au are below detection limits.

**Figure 15.** Trace element patterns of combustion metamorphic ZnS (sphalerite), normalized to its authigenic sedimentary precursor ZnS (würtzite and sphalerite); based on LA-ICPMS (Table 3), SEM-EDS and EPMA (Table 2) data. Cal = calcite, OM = organic matter, Sp = sphalerite, Wur = würtzite.
5.2. CM Marbles: TE Signatures in Sediments and Redox Conditions of Their Annealing

All Tullul Al Hammam CM marbles share certain geochemical similarity (e.g., high P, Zn, Cd, U; elevated to very high Se, Ni, V, Mo; low Fe, As, Sb; very low Mn, Co, Ti, Hg contents), even though individual samples may be different. The major- and trace-element compositions of the marbles, including high Zn up to ~1000–1500 ppm, with abundant Zn oxide and sulfide mineralization (Table 1), are likewise similar because they formed by high-temperature low-pressure alteration of the same sedimentary protoliths [14,19,20,22]. The distribution of redox-sensitive elements (RSEs) in both Muwaqqar Fm. sediments and CM marbles shows high Zn concentrations, while Cd varies from low or moderate to extremely high [4,14,19,20,51]. This feature becomes prominent upon comparison of 20–40 g replicas of the same CM marble sample (nugget effect). According to our data, the difference is within 1.04–1.16 times for Zn and about two or three times for Cd. These patterns, which have been also found common to MVT host rocks, may explain the large range of Cd contents in sphalerite [1,14,85]. Se, Ni, and Cu in CM marbles are likewise unevenly distributed (Table 3), and the nugget effect in metamorphic rocks can thus be attributed to an uneven distribution of authigenic pyrite (the primary host of the respective elements) in the precursor sediments.

The formation of oxide- or chalcogenide-dominated mineral assemblages of Zn, Cd, Ni, and Cu during CM events was mainly governed by local redox conditions. The oxygen supply during burning of disseminated OM and annealing of sediments controlled the activity ratio of sulfidic and sulfate sulfur. At any redox regime, CM alteration of ‘oil shales’ was accompanied by their considerable decarbonation and total dehydration, as well as by partial loss of sulfur and some other highly volatile elements, such as Cd, Hg, and As. Most of the Tullul al Hammam marbles store Zn in oxides [19,20]. The prevalence of oxygenated Zn compounds is reasonable because combustion metamorphism commonly occurs at an excess of the oxidant (air oxygen) over fuel, with oxygen fugacity (fO2) at or above the magnetite/hematite buffer [86–88].

CM alteration of the sedimentary rocks rarely occurs in reduced conditions, at an excess of fuel over oxidant. Nevertheless, diverse sulfides [4,16,19,20], such as zoharite ((Ba,K)6(Fe,Cu,Ni)25S27) [12], K-Fe-Cu-Ni sulfide [5], ZnS, and Ag-S compounds [19,20]; native elements [6]; and phosphides, including halamishite (Ni5P4), negevite (NiP3), transjordanite (Ni3P), and polekhovskyite (MoNiP2), have been progressively more often found in CM rocks of the Mottled Zone [6–11].

Widespread apatite-group minerals record the redox conditions during CM alteration of P-rich sediments [89,90]. Zn-Cd oxide mineralization predominates in the marbles with rock-forming fluorapatite-fluorellesstadite (Ca5(SiO4)1.5(SO4)1.5F)-Ca5(PO4)3F solid solutions, with coupled (SiO4)4- and (SO4)2- groups [18–20,91,92]. In sphalerite marbles, rock-forming Ca phosphate is (SiO4)3-substituted carbonate-fluorapatite poor in sulfate sulfur (0.49–1.85 wt% SO3 in fluorapatites from DT samples) (Figure 6; Table 4). The pristine and pelletal phosphorites from the Muwaqqar Fm. sediments composed of cryptocrystalline carbonate-fluorapatite (francolite) have a composition of 51.4–52.2 wt% CaO, 36.0–37.7 wt% P2O5, 0.5–1.3 wt% SO3, 1.6–3.9 wt% F, 0.2–0.5 wt% Cl, up to 1.5 wt% SrO, and wt% 0.3–0.9 Na2O [14,30], which is consistent with the content of SO3 in CM carbonate-fluorapatite. Formation of a (SO4)2-–rich fluorellestadite member obviously requires additional sulfur sources, such as S-rich II-type kerogen and authigenic sulfides (ZnS and FeS2), in the Muwaqqar Fm. sediments [14].

Conversion of sulfide sulfur to sulfate occurred by oxidative combustion of dispersed S-rich kerogen and sulfides. The same process can destroy the primary depots of TE and thus liberate metals that were immobilized in authigenic sulfides (Zn, Cd, Fe, Ni, Cu, Mo, Ag) or bound with organic matter (Ni, V, Cu). During oxidative annealing of ‘oil shales’, Zn, Cd, Ni, and Cu are immobilized in simple or double (Ca- or Mg-bearing) oxides, or less often form complex compounds, such as tululite [15,18–20,93]. Mo and V oxidize to their highest oxidation states and form the respective anions. Vanadate is mainly consumed by apatite and nabimusaite supergroup minerals [18–20,94]. Molybdate has been found so far as a single mineral of powellite (CaMoO4) in Jordanian CM marbles [4,93]. Silver is off this trend and mainly occurs as halides or sporadically as sulfide and native Ag [18–20,93].
Iron (mainly Fe$^{+3}$) forms complex ferritic phases with Ca, Al, Ti, Cr, and Zr, but Fe$^{+2}$ compounds are of secondary importance, excepting relatively widespread (Mg, Zn, Ni, Cu, Fe)O solid solutions with Zn $\gg$ Ni $\geq$ Cu $>$ Fe$^{+3}$ [5, 6, 15, 19, 38, 93, 95].

Partitioning of iron between different minerals of sphalerite-bearing CM marbles is worth special attention because Fe is a main carrier of sulfidic sulfur under reducing conditions in ordinary metamorphic rocks [3, 73]. Rocks formed at temperatures similar to those for the Jordanian CM marbles contain other Fe-bearing sulfides, besides predominant pyrrhotite. This is specifically the case of the Kochumdek contact aureole with abundant pyrrhotite, less-abundant Fe-rich sphalerite and ramsdellite, and sporadic Mn- and Fe-rich wurtzite [73]. In meteorites, pyrrhotite is likewise a predominant sulfide while sphalerite has the greatest Fe enrichment [72]. Unlike these, FeS or Fe$_2$S$_2$ have been found in none of the Tullul Al Hammam marble sample. The lack of iron sulfides and low Fe contents in the CM sphalerites may be due to a joint effect of low Fe contents in precursor ‘oil shales’ and specific redox conditions during their CM alteration. The original depletion in Fe led to a predominance of authigenic ZnS over FeS$_2$ at prominent excess of sulfide sulfur mainly stored in kerogen [14]. As for the redox regime, both sulfide-bearing and sulfide-free assemblages that form during CM alteration of the Muwaqqar Fm. sediments contain predominant Fe$^{+3}$ compounds, mainly complex calcium ferrites and aluminoferrites.

The temperature and redox conditions of combustion metamorphism are also indicated by complex Ca-Fe-Ni-Cu oxychalcogenides coexisting with sphalerite. Oxysulfide compounds are extremely rare in nature [15, 16, 96] but are ordinary intermediates during calcination roasting of Fe-bearing sulfides. Among these, Ca-Fe oxysulfides Ca$_3$Fe$_4$S$_7$O$_6$ and CaFeSO are the most common and have the largest stability fields. The composition, structure, and stability fields of Ca, Fe$^{2+}$, Fe$^{3+}$, Zn, Cu, and Ni oxysulfides have been well documented because they are key intermediates in industrial carbothermal metal reduction and/or reduction-calcination reactions in metal-sulfur-calcium-oxygen (M-S-Ca-O) systems. A complete set of phases at the intermediate reduction stage of complex Zn, Cu, and Ni sulfide ores includes metals; Fe-Ni alloys; ferrites and aluminoferrites of Ca, CaO, or CaS; as well as Ca and Fe oxysulfides with different stoichiometry [97–104]. The industrial process is performed under ambient pressure and 900 to 1250 °C, in the presence of carbon (C$^0$), CaO/CaCO$_3$, and/or CaSO$_4$. The redox conditions of the process, which is controlled by partial gas pressure of H$_2$S/SO$_2$ and CO/CO$_2$ (commonly expressed as SO$_2$ or CO gas potential or fugacity), provides selective oxidation of Fe$^{+2}$ to Fe$^{+3}$. Iron interacting with CaO binds into oxide (mainly Ca ferrites) and oxysulfide phases and thus becomes separated from the reduced forms of Zn, Cu, and Ni occurring as sulfide or metal phases [97–102].

In the Cu-Fe-Ca-S-O system, no metallic phases have been observed below 850 °C because both Fe and Cu form complex oxysulfides. Under higher temperatures (>900 °C) and f$_{SO2}$ between 10$^{-8}$ and 10$^{-4}$ atm, Cu$^0$ begins to separate and coexist with the CaFeSO phase [99]. Nickel needs a higher f$_{SO2}$ (10$^{-5.5}$–10$^{-5}$ atm at 850 °C and 10$^{-4}$ atm at 1000 °C) for reduction and separation from Fe, which occurs as Fe$^{+2}$ or Fe$^{+3}$ compounds. The very narrow range of f$_{SO2}$ where Ni can reduce selectively requires fine regulation of f$_{SO2}$ and thus impedes Ni separation from Fe. Therefore, (Ni, Fe) alloys frequently occur instead of metallic Ni. Carbothermal reduction using CaO doping at 950 to 1050 °C can make Ni$^0$ separation from Fe more efficient, because iron preferentially reacts with lime forming Ca$_3$Fe$_4$S$_7$O$_6$ and CaFeSO phases and more complex Ca-Fe-Ni oxysulfides [99, 105]. Separation of Ni from Ca-Fe oxysulfides can likewise be achieved by using carbon monoxide as a reducing agent [105].

The discovered assemblages of sphalerite, brownmillerite, Ca ferrites, and mixed oxychalcogenides (with S and Se) of Ca-Fe-Ni-Cu with exsolution textures and micrometer-sized inclusions of Ni, Ag, and Zn phases indicate that carbothermal reduction of metals and reduction-calcination reactions in Me-S-Se-Ca-O systems took place in a natural environment. Oldhamite (CaS), Ca ferrites, and Ca-Fe oxysulfides can coexist at 727 °C in the absence of Fe sulfides, native elements, and magnetite within a very restricted field of the phase diagram of the Ca-Fe-S-O system [97]. It allows one to constrain some physicochemical parameters of the natural process. Theoretically, the FeS-to-CaO ratio of the reacting
mixture during carbothermic metal reduction should be in the range 0.3–0.5. Since the FeS/CaO ratio in bulk iron-depleted sediments is obviously <0.3, oxychalcoenide mineralization in CM rocks is restricted to local spots with the highest contents of S-rich kerogen, Zn, and Fe sulfides in the precursor sediments. Oxygen partial pressure ($f_{O2}$) can be estimated as $\sim 10^{-20}$ atm and the respective $f_{SO2}$ as $\sim 10^{-10}$ atm. No metallic phases have been observed in the Cu-Fe-Ca-S-O system below 850 °C because both Fe and Cu form complex oxysulfide compounds. Under higher temperatures (>900 °C) and lower oxygen fugacity ($f_{SO2}$ between $10^{-8}$–$10^{-4}$ atm), Cu$^0$ begins to separate, and coexists with the CaFeSO phase [99]. These estimates are consistent with the absence of native element species in sphalerite-bearing marbles.

5.3. Trace-Element Patterns of CM Sphalerite

Sphalerite is an important host mineral for a wide range of trace elements in CM rocks (Tables 3, 9 and 10), but only Cd and Se reach abnormally high values of ~14 wt% and ~6.7 wt%, respectively. Both elements are inherited by CM sphalerite from authigenic sulfide minerals: Cd from (Zn,Cd)S modifications and Se from pyrite (Tables 2 and 3) [4,14].

Cadmium in the CM sphalerite that resulted from the clinkering of Zn- and Cd-enriched calcareous marine sediments is 2.01 wt% Cd on average (N = 200) (Tables 3, 9 and 10; Figure 10). This value is much above the common average of Cd contents in sphalerite from economic deposits (0.25–1.1 wt% Cd [1]) and is commensurate with the highest concentrations in that from MVT ores [106], e.g., 1.4 wt% Cd in sphalerite from the Niujiaotang zinc deposit in the Guizhou province of China [85]. Note that the Muwaqqar Fm. marly chalks were considered as immature precursors of MVT deposits [14].

Cadmium contents are lower and the Zn/Cd ratios are higher than in the precursor sediments in the greatest number of the CM marble samples we studied. Namely, the average Zn/Cd ratio is 16 for the marbles and 11 for the Muwaqqar Fm. marly chalks (Table 1). This difference is due to the high volatility of Cd and is well known for combustion of fossil fuels and clinkering of carbonate rocks [14,19,107–109]. Although much Cd becomes lost during annealing of sediments, CM marbles often contain large amounts of cadmium exceeding the bulk sphalerite storage capacity and also bear other Cd accessories, such as (Ca,Cd)O, tululite, greenockite, or very rarely cadmoselite.

CM sphalerites are much more depleted in Cd than authigenic sphalerite or würtzite, with average Cd contents of about 9 wt% (Zn$_{0.83-0.88}$Cd$_{0.07-0.09}$Fe$_{0.01}$Cu$_{0.01}$S sphalerite; Zn$_{0.85-0.88}$Cd$_{0.08}$Fe$_{0.01}$S würtzite; Tables 2, 3, 9 and 10; Figures 10, 14 and 15). Our collection includes a single marble sample (TH-74) with a Zn/Cd ratio as low as 4.4, which contains sporadic sphalerite with an erratic value of Cd reaching ~ 14 wt%, and minor greenockite. This specific case illustrates the general trend that the amount of Cd incorporated into the ZnS$_{cub}$ lattice decreases dramatically as the formation temperature increases, while complete solid solution exists between the ZnS and CdS hexagonal polymorphs [25,71].

The (Zn,Cd)S–T(°C) diagram (Figure 14) illustrates a transition from Cd-rich low-temperature authigenic sphalerite to ultrahigh-temperature Cd-depleted sphalerite from the Kochumdek contact marbles (T $\geq$ 900 °C). The ZnS$_{cub}$ compositions with moderate Cd contents, which represent high-temperature (800–850 °C) sphalerite from the Jordanian CM marbles and those from volcanic fumaroles in the Kuriles (600–750 °C), fall in the middle of the same trend. As it was found out earlier for a Zn-Cd-S-Se system at 1000 and 800 °C [25], zinc blende-type structure exists only in Zn-rich compositions of: $\leq$20 mol% CdS on the ZnS-CdS side and $\leq$ 40 mol% CdSe on the ZnSe-CdSe side, whereas most compounds have a würtzite-type structure. The stability field of the (Zn$_{1-x}$Cd$_x$)(Si$_{1-x}$Se$_x$)$_2$ hexagonal phase expands with temperature from 22 mol% CdS at 600 °C to ~10 mol% CdS at 900 °C [71]. Since the CdS-CdSe diagram is of type I Roozeboom with unlimited miscibility among the components [71], the (Cd,Zn)(S,Se) solid solutions found in the Jordanian CM marbles can be considered as regular ones between CdS$_{hex}$ and CdSe$_{hex}$ (Table 11). Unfortunately, the sizes of greenockite and cadmoselite crystals are too small to characterize their structure directly.
Iron is almost always present in natural sphalerite, varying from trace amounts to 50 mol% FeS (in meteorites only [72]). Commonly, Fe contents in sphalerite increase progressively with the crystallization temperature. High Fe and Mn contents reaching ~19 wt% and ~6.5 wt%, respectively, were observed in sphalerite coexisting with alabandite and pyrrhotite from ultra-high-temperature contact metamorphic spurrite-merwinite marbles, whereas wurtzite in these marbles contains more manganese and less iron (~17 wt% against ~8.5 wt%, respectively) [73]. Quite high Fe contents were also reported for sphalerite from Fe-rich host rocks, namely hedenbergite skarn [1]. Low iron contents in Jordanian CM sphalerite, 1.44 wt% Fe on average (N = 200) (Figure 10), result mainly from low Fe_{total} in the marbles and its preferable fractionation as Fe^{3+} in complex Ca-rich oxides (brownmillerite, srebrodolskite, and other Ca ferrites).

Manganese concentrations in the CM sphalerite are from a few hundred to 1700 ppm, while Co contents are an order of magnitude lower (Table 3). The Mottled Zone CM assemblages lack Mn- and Co-bearing minerals because both elements had very low contents in the precursor sediments. Manganese contents of around 3 wt% MnO were measured only in tululite, a complex Ca-Al-Zn-Cd-Fe-Mn oxide, a single relatively abundant high-temperature Mn mineral found so far in the Mottled Zone complexes [20], besides accessory Mn-enriched spinel of the MgFe_{2}O_{4}–FeMn_{2}O_{4} series reported from CM hornfels in the Hatrurim Basin [93,94,110].

Cobalt contents in the CM sphalerite are quite low (X_{av} = 124 ppm for DT-20 and 66 ppm for DT-25). It is tempting to attribute this depletion to the respective depletion of the protoliths, but the same Co contents are common to other natural sphalerites as well. The Co range in natural sphalerites is commonly from 1 to 840 ppm, except for a few skarn deposits containing up to ~1500–2300 ppm Co [1], though Co^{2+} and Fe^{2+} ions are of similar sizes and intermediate compositions with up to 40 mol% CoS exist among CoS-ZnS solid solutions of zinc blende-type structures [1,111]. Taking into account very low Co contents (commonly ~2 ppm) in the bulk CM marble samples, sphalerite can be expected to be a Co carrier in these rocks.

The contents of nickel (265 ppm) determined by LA-ICPMS in a few quite large homogeneous sphalerite grains from Ni-rich sample DT-25 are within the same range 176–296 ppm as in sample DT-20, which is more depleted in Ni and lacks Ni minerals. The Ni enrichment of the Mottled Zone CM sphalerites is far higher than the <0.1 ppm to 11.4 ppm values measured by LA-ICPMS in other natural sphalerites [1]. Few experimental data indicate the restricted ability of Ni to incorporate into sphalerite even at ~800–850 °C. Wu et al. (1989) [112] revealed restricted NiS-ZnS solid solutions (up to 3 at.% Ni) and confirmed the sphalerite structure of the Zn_{48}Ni_{2}S_{50} phase. The presence of exsolution textures provides reliable evidence that the range of NiS-ZnS solid solutions becomes narrower at lower temperatures. Ni shows a similar behavior upon the cooling of complex oxychalcogenides and forms an exsolution network of an Ni-S-Se phase in the matrix of Ca-Fe-Cu oxysulfide (Figure 8). The contents of Ni in the CM sphalerite are 20 to 30 times as high as those determined by LA-ICPMS in sphalerite from the main economic deposits [1]. Therefore, they appear to be at the highest limit for natural sphalerites.

As it was found out previously [14], type-II kerogen of precursor sediments is the main carrier of V and Ni (up to 50% of bulk Ni content in the rock) along with authigenic pyrite (up to 1.6 wt% Ni). Both sedimentary Ni carriers were involved in the formation of sulfide mineralization during reducing annealing. Note in this respect that trevorite (NiFe_{2}O_{4}) and bunsenite (NiO) have been the only Ni-dominant oxides identified so far in the Mottled Zone CM rocks [7,93,113]. Other oxide accessories with essential Ni contents are spinel-group minerals, periclase, Ca ferrites, and silicoferrites [15,93,114]. On the other hand, more than 10 oxygen-free Ni minerals were found in reducing assemblages from the MZ complexes: kamacite (Fe,Ni) [6]; numerous Ni- and Fe-Ni-phosphides (schreibersite ((Fe,Ni)$_{3}$P), baringerite ((Fe,Ni)$_{2}$P$_{hex}$), murashkoite ((Fe,Ni)P), allabogdanite ((Fe,Ni)$_{2}$P$_{rhom}$), zuktamrurite ((Fe,Ni)P$_{2}$), halamishite (Ni$_{5}$P$_{4}$), negevite (NiP$_{2}$), transjordanite (Ni$_{2}$P), polekhovskyte (MoNiP$_{2}$), nazarovite Ni$_{12}$P$_{3}$ [6,7,9–11,115–118], millerite and/or mäkinenite (Ni(S,Se)) [4,16], zoharite [12], and pentlandite; as well as a number of unidentified Ni phases, including Ni$_{2}$As and K-Fe-Cu-Ni.
This long list has been extended with Ni oxychalcogenides revealed in the Jordanian CM marbles. Thus, Ni manifests high mineral productivity in CM processes under reducing conditions, but it becomes mainly dispersed as impurity in complex accessory oxides upon oxidative combustion.

Silver shows highly uneven distribution in CM sphalerite and has been found by SEM-EDS (within 1–5 wt%) only in grains with microscopic inclusions of Ag minerals (Tables 6 and 7). The LA-ICPMS estimate of 0.42–0.53 ppm Ag for large homogeneous grains (Table 3) appears to be more reasonable for lattice-bound Ag and rules out the role of CM sphalerite as a silver carrier. Meanwhile, the sphalerite structure acquires higher storage capacity with respect to these impurities under peak metamorphic conditions judging by complex exsolution textures with Cu, Ni, and Ag discrete minerals.

Unexpectedly, we discovered relatively high mercury contents of 132 to 226 ppm in CM sphalerite. The precursor sediments are extremely poor in Hg, while most mercury becomes lost during annealing, and its bulk content in marbles is orders of magnitude lower (<0.002 to 0.025 ppm) (Table 1). This discovery has confirmed the inference of Cook et al. (2009) [1] that sphalerite frequently acts as a dominant Hg carrier (Figure 15).

Average contents of indium in CM sphalerite are within a few ppm but are 10 times higher than in authigenic ZnS (Figure 15). No coupling with Cu contents appears, possibly, because the concentrations are too low.

Like previous workers [1], we failed to discover an incorporation of Cu, Ga, and Pb in CM sphalerite and to find even trace amounts of Ge, Sn, Mo, Ti, and Au. Judging by the contents of Ga, Ge, Mo, Ag, and Pb (hundreds of ppm) and about 7800 ppm Cu in the sedimentary ZnS precursors (Table 3; Figure 15), the TE composition of the high-temperature ZnS phase became much simpler during annealing. In most of the analyzed samples, sphalerite compositions are uniform both within (no zoning) and between grains, with minor standard deviations in element concentrations (Table 10). The only exception is in the mineral diversity of sample DT-25, which, to a high probability, mirrors the primary heterogeneous distribution of TE hosts in the parent sediment.

Unlike authigenic ZnS, which contain about 2000 ppm As and Sb, CM sphalerites are depleted in both elements (Figure 15). Trace amounts of Bi were detected in authigenic ZnS, but its content is below the detection limit in CM sphalerite. Tellurium is also below the detection limit in both authigenic and metamorphic ZnS. Thus, Se is the only anionic element occurring in a significant concentration in the CM sphalerite (Tables 3, 9 and 10; Figures 10 and 15).

The sphalerites from the Jordanian CM marbles contain at least 0.29 wt% Se (Table 10; Figure 10), and the Se contents in most of the sphalerite grains we analyzed (~80%) are from 0.3 to 1.9 wt% Se. The concentrations exceeding 2 wt% Se (reaching 6.68 wt%) are restricted to sphalerite associated with Ni and Ag selenides, as well as with Se-rich complex oxychalcogenides (sample DT-25). SEM-EDS and elemental mapping revealed a homogeneous distribution of Se within individual CM sphalerite grains at notable variations among grains in thin sections.

Although complete solid solutions exist between cubic modifications of ZnS and ZnSe (stilleite) under the conditions of high-temperature dry synthesis (800 and 1000 °C) [25], the Se concentration in natural sphalerites rarely reaches thousands ppm. They are namely sphalerites from black shales and some skarn or epithermal deposits, which have smooth profiles indicating lattice-bound Se [1]. As in our case, abnormal Se concentrations were reported for sphalerites that were associated with selenides and contained inclusions of Se-bearing minerals revealed by Se spikes in LA-ICPMS profiles [1].

The comparison of TE compositions of authigenic and CM sulfides reveals moderate Se fractionation in the sphalerite structure under high-temperature (800–850 °C) dry reducing conditions. The assemblages in sample DT-25 demonstrates that Se preferably fractionates into Ni and Ag selenides and complex oxychalcogenides but remains only an impurity in the coexisting sphalerites. Furthermore, the incorporation of large Se amounts (>2 wt%) in sphalerite is rigorously controlled by extremely high bulk Se contents within local rock volumes. However, the content of Se in CM sphalerite becomes 15–50 orders of magnitude higher than in the Se-poor sedimentary ZnS precursors.
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(Figure 15). In the marbles, clusters of selenides; Se-bearing Zn, Ni, and Ag sulfides; and Fe, Ni, and Cu oxychalcogenides formed at the expense of Se-bearing pyrite and S-rich kerogen clots.

In general, the composition of the Jordanian CM sphalerite with comparable average concentrations of Cd, Se, and Fe at >1 wt% may be characterized as ‘extreme’ according to [1]. In the previous sections of this discussion, we considered the structural and chemical reasons for substitutions, ranges of solid solutions, and main trends of TE fractionation in high-temperature dry moderately reducing CM environments. However, discrimination between lattice-hosted elements and those in nano- and micro-scale inclusions is not always possible, even by SEM, EPMA, and LA-ICPMS techniques [1]. Below, we discuss the distribution patterns of elements in the structure of real sphalerite crystals using the data of single-crystal XRD and Raman spectroscopy.

5.4. Crystal Structure and Distribution of Cd, Fe, Se, and O in CM Sphalerite

The lattice parameters of binary mixed compounds often conform to simple regularity and depend linearly on the composition, which is particularly valid for ZnS-CdS$_\text{cub}$, ZnS-ZnSe$_\text{cub}$, and ZnS-FeS$_\text{cub}$ solid solutions [25,61,66,71]. However, the miscibility of several substances (multinary mixed phases) on the scale of more than a few per cent is not very frequent, apart from intermetallic systems, and each specific case requires proofs [25].

Single-crystal XRD has provided direct evidence for the distribution of Cd, Fe, and Se in CM sphalerite. The analyzed crystal did not show any additional reflections that would represent inclusions or domains of extraneous phases, whether Cd, Fe, and Se or O-bearing compounds, such as ZnO or Zn sulfates. Thus, the sphalerite is single crystal, and the compound is a multinary mixed phase, with the main impurities randomly distributed in the structure. Following the common practice [26,119,120], we applied the single-crystal XRD method to estimate the amount of oxygen in sphalerite.

The analyzed sphalerite of the complex composition Zn$_{0.96}$Cd$_{0.02}$Fe$_{0.02}$(S$_{0.946(8)}$O$_{0.046(8)}$Se$_{0.0074}$)$_{\Sigma 1.00}$ has a smaller unit cell than pure ZnS (5.40852(12) Å against 5.4094 Å [56]) (Table 12), explainable only by the substitution of O$^{2-}$ (1.40 Å) for S$^{2-}$ (1.73 Å). Each revealed substitution is individual, because otherwise they jointly would increase the $a$-parameter of the sphalerite (e.g., 5.411 Å at a mole fraction of 0.02 for FeS [60,61,121]), given that both Fe$^{2+}$ and Cd$^{2+}$ are larger than Zn$^{2+}$ (0.64, 0.78, and 0.60 Å, respectively), while Se$^{2-}$ likewise has a larger radius (1.84 Å) than S$^{2-}$ (1.73 Å).

The sphalerite contains around 0.5 mol% ZnO, and its $a$-parameter, in the absence of other isomorphic substitutions, should be 5.4077 Å assuming the structure reduction from 5.4081 Å at 0.4 mol% ZnO to 5.4065–5.4070 Å at 0.8 mol% ZnO upon the oxygen-for-sulfur substitution reported by [58]. Its difference from the unit cell of pure ZnS is slightly compensated by the presence of large Cd, Fe, and Se ions.

Natural sphalerite of the complex composition (Zn,Cd,Fe)(S,O,Se) can be expected to crystallize in the zinc blende structure F43m (Td$^2$) (Table 12) by analogy to what was inferred for Zn-dominated (Zn$_{1-x}$Fe$_x$)$_2$SiO$_4$ solid solution [61]. However, the Raman spectra of our sample are more complex and contain strong bands at 299, 309, and 331 cm$^{-1}$ in addition to the predicted bands common to ZnS$_\text{cub}$ (Table 13; Figures 11 and 12).

Theoretical analysis of the solid solution suggests either one- or two-mode transformations between phases. The mineral we studied has an intermediate composition. In the case of one-mode transformation, the composition change leads to respective changes in the frequency of selected bands. This is, for instance, one-mode behavior of olivine (Mg$_{1-x}$Fe$_x$)$_2$SiO$_4$ in an Fe-Mg cationic solid solution, where x is the mole fraction of Fe. At a two-mode phase transition, the frequency of the bands changes continuously or sometimes stepwise. In the latter case, one or more new vibration bands appear at some critical content x, usually in the same spectral range, whereby the mode intensity pumps from the initial band to the new band(s) as x changes. The behavior of the zinc blende (Zn$_{1-x}$Fe$_x$)$_2$SiO$_4$ solid solution rather corresponds to the two-mode model: As the Fe content changes, the Raman spectra change correspondingly, first continuously and then stepwise, starting from x = 0.1 [61]. The behavior
of the (Zn,Cd,Fe)(S,Se,O) complex solid solution in our case fits neither of the two previous models but is rather multi-modal. This is evident in three strong modes that appeared at increasing x.

The vibration states of the ZnS<sub>cub</sub>, FeS<sub>cub</sub>, and CdS<sub>cub</sub> endmembers of the Zn-Fe-Cd solid solution were calculated with the LADY software for lattice-dynamic simulations. According to the simulations, strong LO bands should appear in the first-order Raman spectra: 350 cm<sup>-1</sup> for cubic ZnS (sphalerite), 359 cm<sup>-1</sup> for cubic FeS (rudashevskite), and 324 cm<sup>-1</sup> for cubic CdS (hawleyite). However, the observed spectrum misses two latter bands, which proves the absence of FeS<sub>cub</sub> and CdS<sub>cub</sub> discrete phases exsolved from the parent homogeneous solid solution, as well as a statistical distribution of Zn, Fe, and Cd cations at the same positions of the mineral structure.

The homogeneity of the studied crystals revealed by the spatial micro-Raman analysis characterizes the solid solution as regular. Judging by the high content of oxygen in the sample, it may contain Zn- and O-bearing microscopic inclusions or layers/films in the ZnS matrix. Zinc oxide (ZnO) can exist either as hexagonal zincite (würtzite type) or cubic (zinc blende-type) modifications. The Raman spectra of zincite should include additionally a sharp band at about 437 cm<sup>-1</sup> (TO) and another wide band at 524 cm<sup>-1</sup> (LO) with a 562 cm<sup>-1</sup> shoulder (RRUFF, R060027 card); in the case of ZnO<sub>cub</sub>, additional bands may appear at about 340 (TO) and 525 cm<sup>-1</sup> (LO) [122,123]. However, none of these bands were observed in our sample. The vibration modes of the cubic modifications are known [122] to have the same frequencies as those of the hexagonal phase and generally cannot be used for discrimination between the two structures. Therefore, our data suggest that O<sup>2−</sup> may substitute for sulfur in regular sites of the ZnS cubic cell, and its position is averaged.

Thus, single-crystal XRD and Raman spectroscopy concordantly indicate that the natural crystal of the complex composition (Zn,Cd,Fe))(S,Se,O) is isostructural with sphalerite and has a disordered distribution of all main impurities in the ZnS<sub>cub</sub> lattice. This appears to be the first proof that a restricted ZnS<sub>1−x</sub>O<sub>x</sub> solid solution can form in nature.

5.5. Oxygen in ZnS Compounds: Experimental Background and Crystal-Growth Practice

Among the VIB subgroup chalcogens, oxygen most strongly differs from S, Se, and Te, which it replaces; the incorporation of even minor amounts of O can cause significant local changes to the lattice of chalcogenides and to the properties of their composites. Chalcogens differ from oxygen in greater Pauling electronegativity (3.44 against 2.58 for S, 2.55 for Se, and 2.1 for Te) and lower polarizability (3.88×10<sup>-23</sup> cm<sup>3</sup> for O<sup>2−</sup> against 10.2×10<sup>-24</sup> cm<sup>3</sup> for S<sup>2−</sup>, 10.5×10<sup>-24</sup> cm<sup>3</sup> for Se<sup>2−</sup>, and 14.0×10<sup>-24</sup> cm<sup>3</sup> for Te<sup>2−</sup>) [66]. This dissimilarity entrains differences in the crystal chemistry of oxides and chalcogenides for nearly all element combinations and restricts isomorphic substitutions between S<sup>2−</sup> and O<sup>2−</sup>. Nevertheless, it is well known that limited amounts of oxygen can substitute for isovalent S<sup>2−</sup> in chalcogenides [66].

The possibility of O incorporation into sulfides was checked for the first time by Skinner and Barton [58], who synthesized oxygen-substituted sphalerite and würtzite (with 0.7 wt% and 1.0 wt% ZnO, respectively). However, the O<sup>2−</sup> → S<sup>2−</sup> substitution in natural minerals is hard to prove unambiguously even nowadays. In the case of ZnS, this is especially difficult because ZnS<sub>hex</sub> and ZnO belong to the same structure type (würtzite) and share similarity in the parameters of flat nets in the two phases, which favors their epitaxial co-crystallization. This feature has been employed in the practice of industrial synthesis of semiconductors as the growth of a ‘layered cake’ consisting of alternated nanometer layers of ZnS<sub>hex</sub> and ZnO that have different conductivity types [27].

The ternary semiconductor alloys of II-VI groups, with their large energy band gap and binding energy of excitons, are of growing interest for uses in optoelectric devices operating in the visible and ultraviolet spectral regions. They are specifically ZnS, ZnO, and their dilute ternary alloys ZnS<sub>1−x</sub>O<sub>x</sub> having semiconducting properties [124]. The diverse applications of ZnS crystals and films in various high-tech devices (solar cells, electroluminescent diodes, dielectric filters, etc.) induced investigations into the interactions of ZnS (both sphalerite and würtzite) with oxygen during the synthesis and oxidation of ZnS composites exposed to air. The studies revealed three main
modes of oxygen occurrence in ZnS phases: (i) restricted solid solutions ZnS\(_{1-x}\)O\(_x\) (lattice oxygen); (ii) heterophase CVD films (combination of ZnS, ZnO, and Zn(OH)\(_2\) films and Zn sulfates); (iii) surface oxidation of ZnS during annealing or operation which produces Zn sulfate films [28,120,125].

It appears pertinent to compare the scale of O\(^2^-\) \(\rightarrow\) S\(^2^-\) substitutions in synthetic and natural CM sphalerites, because our single-crystal XRD and micro-Raman spectroscopy results revealed no extraneous phases in the CM sphalerite crystals but proved the presence of lattice-bound oxygen.

The incorporation of oxygen atoms into the ZnS structure leads to dramatic changes of the band pattern and related fundamental properties, which makes the alloys technologically important [28,120]. Much effort was put into constraining the stability fields of the phases where sustainable synthesis of such crystals is possible: ZnO doped with S\(^2^-\) and ZnS doped with O\(^2^-\). There is a large miscibility gap between ZnO (würtzite type) and ZnS (sphalerite type) due to their structural difference at temperatures below 1020 °C and to the considerable difference of the S\(^2^-\) and O\(^2^-\) radii (1.73 and 1.40 Å, respectively). The ZnO-ZnS system exhibits an approximately symmetrical region of immiscibility between 5 and 96 mol\% ZnS at 900 °C. XRD of single crystals and polycrystalline samples indicates that ZnO\(_{1-x}\)S\(_x\) and ZnS\(_{1-x}\)O\(_x\) phases with x between 0.0 and 0.05 are thermodynamically stable at 900 °C [26]. The ZnS\(_{1-x}\)O\(_x\) zinc blende crystals with an oxygen content of x = 0.03125 to 0.0625 were synthesized by Belouche et al. [28]. The thermodynamic stability and electronic properties of würtzite and zinc blende ZnS\(_{1-x}\)O\(_x\) phases were also studied theoretically with first-principle simulations [27] and a composition–temperature (x-T) diagram was plotted for the Zn-S-O system. The results show that the formation enthalpy of würtzite and sphalerite structure types of ZnS\(_{1-x}\)O\(_x\) alloys with randomly distributed O atoms increases steeply as a function of x. This produces spinodal curves for both ZnS\(_{1-x}\)O\(_x\) structural types and limits the stability fields to the compositions near the ZnS and ZnO endmembers (at x < 0.1). For example, the solubility limit was less than 2% at a temperature of 1000 K [27].

Oxygen in the structure of stoichiometric sphalerite commonly occurs as solitary atoms. It is statistically distributed in lattice nodes and is interpreted as dissolved [O\(_3\)]. O\(_3\) close to the limit concentration coexists with excess Zn in the ZnS crystals, where excess Zn can exist as a donor in oxygenated SA complexes [120]. The concentration of [O\(_3\)] in synthetic sphalerite reaches \(\approx\)1.3 wt% near the temperature of the ZnS\(_{\text{sub}}\) ➔ ZnS\(_{\text{hex}}\) transition (1020–1040 °C). In the region of homogeneous solid solutions ZnS\(_{1-x}\)O\(_x\), the range of dissolved oxygen (O\(_3\)) contents spans about three orders of magnitude: from (2–3) \(\times\) 10\(^{20}\) cm\(^{-3}\) in compounds with Zn excess relative to the stoichiometric ZnS composition, at the temperature of 940 to 1060 °C. Without additional doping, O\(_3\) is at a level of 10\(^{17}\)–10\(^{18}\) cm\(^{-3}\) in ZnS crystals and about 10\(^{19}\)–10\(^{20}\) cm\(^{-3}\) in polycrystalline ZnS compounds [120].

The amount of lattice-bound and randomly distributed oxygen revealed by single-crystal XRD in high-temperature (\(\approx\)800–850 °C) natural sphalerite of the Zn\(_{0.96}\)Cd\(_{0.02}\)Fe\(_{0.02}\)(S\(_{0.996(8)}\)O\(_{0.046(8)}\)Se\(_{0.007(4)}\)) composition is in the range of 0 < x < 0.05 inferred for ZnS\(_{1-x}\)O\(_x\) single crystals stable at T \(\approx\) 900 °C.

6. Conclusions

1. Sphalerite from the Tulul al Hammam area in central Jordan is a chief sulfide mineral in combustion metamorphic (CM) marbles that formed after the Maastrichtian-Paleocene bioproductive ‘oil shales’ with abundant authigenic ZnS mineralization: würtzite and sphalerite highly enriched in Cd, Cu, As, Ga, Ge, Ag, and Sb and less-abundant pyrite bearing Ni, Cu, As, S\(_e\), Mo, and Ag. The precursor chalky sediments were annealed by spontaneous combustion of disseminated S-rich organic matter at the parameters of sanidinite facies metamorphism: \(\approx\)800–850 °C, ambient pressure, and a moderately reduced environment.

2. High-temperature annealing of the sediments had several consequences: Recrystallization of authigenic würtzite and sphalerite; total consumption of pyrite; and compositional and textural homogenization of CM sphalerite, whereby the latter acquired a trace-element composition less diverse than in the precursor ZnS. Sphalerites from particular geological environments, such as CM marbles, belong to a single generation; they became compositionally equilibrated and were quenched
near the peak temperature of combustion metamorphism. The Se-rich, and Ni- and Cu-bearing heterogeneous mineral assemblages rarely found in these rocks may, to a high probability, record the primary heterogeneous distribution of TE hosts in the sedimentary protolith.

3. In spite of high formation temperatures, the analyzed CM sphalerites have low Fe but high Cd contents ($X_{\text{av.}} = 1.4\%$, $X_{\text{max}} = 3.7\%$ and $X_{\text{av.}} = 2.0\%$, $X_{\text{max}} = 14.0\%$, respectively) concordantly with the Muwaqqar Fm. marly chalk, which are Fe-poor but rich in Zn and Cd. This effect becomes still more prominent due to iron oxidation during the annealing of sediments. The greatest part of iron in the marbles occurs as Fe$^{3+}$ hosted by Ca ferrites or aluminate ferrites. The CM sphalerites also inherited Se ($X_{\text{av.}} = 1.5\%$, $X_{\text{max}} = 6.8\%$ Se) from the precursor sediments. Another feature is that they have low and relatively stable concentrations of Cu, Ga, In, Sn, and Sb while the Ge, As, Mo, Te, Tl, Bi, Pb, and Au contents are below detection limits. These signatures are not universal for all high-temperature low-pressure metamorphic sphalerites but instead represent a local geological setting.

4. Under the CM conditions (one-stage high-temperature dry annealing and rapid quenching), which are very similar to the experimental conditions of pyrosynthesis, fractionation of trace elements into sphalerite is mainly controlled by crystal structures. This fractionation is limited, though continuous or restricted solid solutions exist in the Zn-Me-S-Se systems (Me = Fe, Cd, Ni, Co, Cu, Ga, and In) at high temperatures. At the same time, Fe, Cd, Se, Ni, and Cu also form their own phases in the CM marbles.

5. Single-crystal XRD and Raman spectroscopy data provide consistent evidence that natural crystals of the (Zn,Cd,Fe)(S,O,Se) composition are isostructural to sphalerite and have disordered distributions of all main impurities, which are lattice bound. This appears to be the first proven case of a ZnO-ZnS restricted solid solution that has formed in nature within the stability field corresponding to a ZnS$_{1-x}$O$_x$ (0 $< x \leq$ 0.05) homogeneous compound at 900 $^\circ$C.

6. As we found out, sulfides and oxychalcogenides can be used for petrogenetic interpretation as sensitive and independent tracers of CM conditions (temperature, redox regime) and metal sources, at least for quickly quenched anhydrous sanidinite-facies rocks.

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