



# The importance of minerals in coal as the hosts of chemical elements: A review



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## ABSTRACT

Coal is a complex geologic material composed mainly of organic matter and mineral matter, the latter including minerals, poorly crystalline mineraloids, and elements associated with non-mineral inorganics. Among mineral matter, minerals play the most significant role in affecting the utilization of coal, although, in low rank coals, the non-mineral elements may also be significant. Minerals in coal are often regarded as a nuisance being responsible for most of the problems arising during coal utilization, but the minerals are also seen as a potentially valuable source of critical metals and may also, in some cases, have a beneficial effect in coal gasification and liquefaction.

With a few exceptions, minerals are the major hosts of the vast majority of elements present in coal. In this review paper, we list > 200 minerals that have been identified in coal and its low temperature ash, although the validity of some of these minerals has not been confirmed. Based on chemical compositions, minerals found in coal can be classified into silicate, sulfide and selenide, phosphate, carbonate, sulfate, oxide and hydroxide, and others. On the basis of their abundance, they can be classified into common, uncommon, and rare. Elements associated with silicates are largely benign, but many of those associated with sulfides and selenides are toxic to the environment and human health (e.g., S, As, Hg, Tl, Se, and Pb). Critical elements, e.g., rare earth elements and Y, Ga, and Al, are mostly associated with clays, phosphate, and carbonate minerals. There are many unusual mineral phases, such as native W, Au, Ag, and various Pt phases, which may have economic and geochemical significance in coal. Although the modes of mineral occurrence of a number of elements have been widely investigated, there are some elements whose associations, and, in particular, association mechanism with minerals are, to a degree, uncertain or even largely unknown and deserve further attention.

## 1. The significance of minerals in coal

Coal may be the most complex geologic material. In addition to the organic matter, valued for its energy potential, all coals contain water, minerals, most, if not all, of the elements in the Periodic Table, oil, gas, rock fragments, and fossils. None of these ancillary components have an impact as significant as do the minerals. Although the statement by Wert et al. (1987) “perhaps every mineral known to mankind could be found in coal” is an exaggeration, coal may indeed contain the largest variety of minerals in nature, based on the numerous publications of minerals found in coal.

From an academic point of view, minerals in coal are useful indicators of paleoenvironments and geologic evolutions, mainly because they may contain detailed and long-term records, which were produced

during syngenetic stages and in many cases were subsequently altered during diagenesis and epigenesis (Dai and Chou, 2007).

Minerals play a significant role in affecting the utilization of coal, from mining to grinding to combustion and technological problems, from coal cleaning to waste disposal, and from the environmental impacts to human health consequences. The minerals reduce the economic value of the coal they are in by diluting the energy content and add expense when removed by coal cleaning processes, whose primary purpose is to remove the minerals prior to combustion or coke production.

The minerals are the primary source of fly ash particles, bottom ash, and boiler slag, and they contribute to the flue gas desulfurization sludge. The minerals also contribute to fouling, slagging, agglomeration, corrosion, and erosion of the boiler (Raask, 1985), which may be

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so severe as to require shutdown of the boiler and costly clean-up procedures. Raask (1985) notes that the minerals in coal had a major influence on early boiler design. Pulverized-coal-fired systems were designed to minimize the time that minerals were exposed to high temperatures, thus reducing fouling and slagging problems. Other boiler innovations, such as slag taps and cyclone-fired boilers, addressed the formation of slag from molten minerals, though minerals are still the primary components in boiler fouling and slagging deposits. Some minerals, primarily quartz and to a lesser extent, pyrite, are responsible for the costly abrasion and erosion of mining and grinding equipment. Proper disposal of the mineral-rich by-products, such as fly ash, coal cleaning wastes, fouling and slagging deposits, bottom ash, and flue gas desulfurization (FGD) residues, adds substantial costs to the use of coal.

During mining, mineral matter may affect roof stability (particularly clay minerals with swelling nature; Mark and Molinda, 2005; Kang et al., 2015; Li et al., 2016b) and cause erosion of mining equipment and frictional ignition of methane. Clays may give rise to handling problems during coal preparation and transport (French, 2018). In fluidised bed combustors, the occurrence of low-melting temperature minerals may lead to bed agglomeration and collapse of the fluidised bed, resulting in boiler shutdown (French, 2018).

Minerals may have adverse effect on coal gasification (Liu et al., 2019). Slag viscosity is a critical parameter in the operation of slagging gasifiers. If the critical viscosity is too high, fluxing agents may need to be added, increasing the cost of the operation. Conversely, if the viscosity is too low, a protective slag coating will not form on the walls of the gasifier and increased erosion of the tap hole may also occur. In Lurgi gasifiers, the occurrence of low melting point minerals may result in ash handling issues, possibly leading to shutdown of the gasifier (French, 2018).

During coal liquefaction, abrasive minerals may lead to increased wear of the coal slurry pumps. However, clays such as smectite, may have a beneficial cracking effect on the liquefaction product, and iron sulphides are known to catalyse the liquefaction process. In coke making, the presence of minerals, such as apatite and pyrite, provide elevated content of phosphorus and sulfur resulting in production of poor-quality iron. The conversion of quartz to cristobalite in the coke may result in fracturing and weakening of the coke. Calcium- and Fe-bearing minerals may also affect coke reactivity.

Minerals contribute to human health issues not only from minerals themselves but also from toxic elements hosted by minerals. Huang et al. (2006) concluded that inhalation of fine-grained pyrite by coal miners was an important causative factor in Coal Workers Pneumoconiosis (Black Lung Disease). Tian (2005), Tian et al. (2008), and Large et al. (2009) concluded that nano-quartz in coal that was being used domestically in Xuan Wei County, Yunnan, Province, China, was the principle cause of the world's highest rate of women's lung cancer. Dai et al. (2008b) showed that exceedingly high levels of quartz (57.6–74.7%, mean 65.7% on a low-temperature ash basis) accounted for the majority of minerals in Xuan Wei coals. Some minerals, sulfides in particular, are the major hosts of toxic elements (such as As and Hg), which have adverse effects on human health (e.g., arsenosis in Guizhou Province, southwestern China) and the environment.

Although the occurrence of minerals in coal is usually regarded as having deleterious effects in coal utilization, minerals in coal have some important beneficial aspects. Coal and coal ash are attracting increasing attention as potential sources of critical elements, such as rare earth elements and Y, Li, Ga, Se, Zr, and Nb (Seredin and Finkelman, 2008; Bullock et al., 2018; Dai and Finkelman, 2018; Lin et al., 2018b; Zhao et al., 2018), all of which are in demand in the semi-conductor industry and the production of advanced materials. In a number of countries, rare earth element concentrations are sufficiently high in the coal ashes to make extraction an economically viable option (Seredin and Dai, 2012; Hower et al., 2016; Kolker et al., 2017a; Laudal et al., 2018; Lin et al., 2018a; Wagner and Matiane, 2018). High-Al coals have also

attracted much attention in recent years in China, because the derived ash has  $\text{Al}_2\text{O}_3$  higher than 50 wt% and thus have been used for Al extraction (Seredin, 2012; Dai et al., 2018d). With a few exceptions (e.g. Ge and U), most of the critical elements are largely hosted in minerals.

A number of papers have discussed the associations between elements and minerals in coal (e.g., Chou, 2012; Kolker, 2012; Ward, 2016; Dai et al., 2018d; and, in particular, Swaine, 1990). In this paper, we identify the most likely minerals or mineral groups that act as hosts for a large number of elements and, when appropriate, we will point out the significance of these relationships. Some of this discussion is based on results from a paper on the quantification of the modes of occurrence of 42 elements in coal (Finkelman et al., 2018). In that paper, the authors concluded that, in bituminous coal, the bulk (> 50%) of all elements except Br were associated with minerals. In low rank coals, a greater proportion of the elements are organically associated, but the majority of the elements still have primary inorganic associations. The exceptions are Be, Br, Mg, Se, Na, and U, and possibly Co, Ni, and Sr. We fully recognize that there are many exceptions to these relationships. For instance, coals with ash yields < 10% many have the bulk of their elements organically associated. Clearly a greater proportion of many elements in low rank coals are associated with the organic matter. Also, coals formed under unusual conditions or influenced by unusual circumstances (oxidation, epigenesis, igneous intrusion, volcanic ash deposits, marine incursion, etc.) may deviate from these generalizations. However, we contend that these coals are the exceptions and that our observations are relevant to the majority of coals mined around the world. Furthermore, almost all elements associate with more than one mineral or even multiple minerals and mineral groups, making unequivocal associations virtually impossible. We try to make the distinction between those elements that are physically associated with a mineral group, i.e., an element in a mineral that is enmeshed in another mineral phase, and elements that are chemically associated with a mineral or mineral group, i.e. part of the mineral structure.

## 2. Minerals found in coal

There are a number of methods to detect and identify minerals in coal. Bulk chemical analysis provides clues as to what minerals or mineral groups may be present in the coal sample. Optical petrography and X-ray diffraction (XRD) can help identify specific minerals (Ward, 2016) but provide little to no information on the trace elements associated with the minerals. Further analysis on XRD spectrum using Rietveld-based interpretation software, e.g., Siroquant, can quantitatively determine the mineral percentages in coal and/or low temperature ash (Ward et al., 2001a, 2001b; Ruan and Ward, 2002; Dai et al., 2012b). Selective leaching helps identify mineral groups such as carbonates (leached by HCl), sulfides (leached by  $\text{HNO}_3$  or HCl), and silicates (leached by HF) and provides information on which elements may be associated with each mineral group rather than specific minerals (Riley et al., 2012; Finkelman et al., 2018; Liu et al., 2015, 2018). Microbeam methods (scanning electron microscopy (SEM), electron microprobe analysis, ion probes, transmission electron microscopes and related instruments) with energy or wavelength dispersive (EDS/WDS) detectors are the most useful method for identifying the host or hosts of the elements in coal (Dai et al., 2012a, 2012b; Etschmann et al., 2017; Hower et al., 2018a, 2018b; Wang et al., 2018; Wei et al., 2018), and in many cases can unequivocally identify a specific mineral unless polymorphs exist. Float-sink density separation combined with XRD, SEM-EDS, and other chemical analyses to determine minerals and trace elements in different density fractions has also been applied (Wagner and Tlotleng, 2012; Tian et al., 2014). Comparison of results for element affinities determined by density separation and selective leaching techniques applied to the same coal showed good agreement for most elements (Querol et al., 2001).

Statistical analyses, e.g., correlation and cluster analyses, have been used to deduce the modes of occurrence of major and trace elements in

**Table 1**

Minerals reported in coal and coal low temperature ash (LTA). The data is taken primarily from Finkelman (1981) and Ward (2016) but with additional information from various sources. The minerals in bold have been confirmed by X-ray diffraction, a unique chemistry, or multiple observations. The validity of those in *italics* has not been confirmed.

| Class     | Mineral             | Formula                                          | Abundance | Comment | Sources                                                           |
|-----------|---------------------|--------------------------------------------------|-----------|---------|-------------------------------------------------------------------|
| Elements  | <b>Gold</b>         | Au                                               | Rare      |         | Finkelman et al. (1979), Seredin and Finkelman (2008)             |
| Elements  | <b>Diamond</b>      | C                                                | Rare      |         | This study                                                        |
| Elements  | Sulfur              | S                                                | Rare      |         | Stutzer (1940), Chou (2012)                                       |
| Sulfides  | Bornite             | Cu <sub>5</sub> FeS <sub>4</sub>                 | Rare      |         | Swaine (1967, 1975), Li et al. (2008), Hower et al. (2018b)       |
| Sulfides  | Argentite           | Ag <sub>2</sub> S                                | Rare      |         | Finkelman et al. (1979), Seredin and Finkelman (2008)             |
| Sulfides  | Pentlandite         | (Fe,Ni) <sub>9</sub> S <sub>8</sub>              | Rare      |         | Belkin et al. (2010)                                              |
| Sulfides  | Chalcopyrite        | CuFeS <sub>2</sub>                               | Common    |         | Hower et al. (2018b)                                              |
| Sulfides  | Greenockite         | CdS                                              | Rare      |         | Karayigit et al. (2000b)                                          |
| Sulfides  | <i>Covellite</i>    | CuS                                              | Rare      |         |                                                                   |
| Sulfides  | Sphalerite          | ZnS                                              | Common    |         |                                                                   |
| Sulfides  | Pyrrhotite          | Fe <sub>1-x</sub> S                              | Rare      |         | Finkelman et al. (1979), Vassilev et al. (1994), Yossifova (2007) |
| Sulfides  | Millerite           | NiS                                              | Uncommon  |         | Lawrence et al. (1960), Dai et al. (2015f)                        |
| Sulfides  | Galena              | PbS                                              | Common    |         | Dai et al. (2006a)                                                |
| Sulfides  | Se-bearing galena   | Pb(Se,S)                                         | Rare      |         | Dai et al. (2007)                                                 |
| Sulfides  | Alabandite          | MnS                                              | Rare      |         | Finkelman (1981), Dvornikov (1990)                                |
| Sulfides  | Cinnabar            | HgS                                              | Rare      |         | Finkelman et al. (1979)                                           |
| Sulfides  | <b>Linnaeite</b>    | Co <sup>2+</sup> Co <sup>3+</sup> S <sub>4</sub> | Uncommon  |         | Coveney et al. (1994)                                             |
| Sulfides  | <i>Polydymite</i>   | Ni <sup>2+</sup> Ni <sup>3+</sup> S <sub>4</sub> | Rare      |         | Dai et al. (2015f)                                                |
| Sulfides  | Siegenite           | (Ni,Co) <sub>3</sub> S <sub>4</sub>              | Rare      |         | Havey and Ruch (1984), Bouška and Pešek (1999)                    |
| Sulfides  | <i>Greigite</i>     | Fe <sub>3</sub> S <sub>4</sub>                   | Rare      |         | Finkelman (1981), Karayigit et al. (2000a)                        |
| Sulfides  | Bismuthinite        | Bi <sub>2</sub> S <sub>3</sub>                   | Rare      |         | Karayigit et al. (2000b)                                          |
| Sulfides  | Stibnite            | Sb <sub>2</sub> S <sub>3</sub>                   | Rare      |         | Hower et al. (2000), Seredin and Finkelman (2008)                 |
| Sulfides  | <i>Molybdenite</i>  | MoS <sub>2</sub>                                 | Rare      |         | Dai et al. (2015f)                                                |
| Sulfides  | Cattierite          | CoS <sub>2</sub>                                 | Rare      |         |                                                                   |
| Sulfides  | <b>Pyrite</b>       | FeS <sub>2</sub>                                 | Common    |         | Querol et al. (1989), Kolker (2012)                               |
| Sulfides  | <b>Marcasite</b>    | FeS <sub>2</sub>                                 | Uncommon  |         | Ding et al. (2001)                                                |
| Sulfides  | <b>Arsenopyrite</b> | FeAsS                                            | Rare      |         | Sarofim et al. (1977), Finkelman (1995)                           |
| Sulfides  | <i>Ullmannite</i>   | NiSbS                                            | Rare      |         | Cech and Petrik (1973), Brownfield et al. (2005)                  |
| Sulfides  | <i>Realgar</i>      | α-As <sub>4</sub> S <sub>4</sub>                 | Rare      |         | Cech and Petrik (1973), Ding et al. (2001)                        |
| Sulfides  | <i>Orpiment</i>     | As <sub>2</sub> S <sub>3</sub>                   | Rare      |         | Dai et al. (2006b)                                                |
| Sulfides  | Gerschellite        | AsSbS <sub>3</sub>                               | Rare      |         | Dvornikov (1990), Finkelman (2003)                                |
| Selenides | Tienmannite         | HgSe                                             | Rare      |         | Dai et al. (2015f)                                                |
| Selenides | <b>Eschbornite</b>  | CuFeSe <sub>2</sub>                              | Rare      |         |                                                                   |
| Selenides | <b>Clausthalite</b> | PbSe                                             | Common    |         |                                                                   |
| Selenides | <b>Krutaite</b>     | CuSe <sub>2</sub>                                | Rare      |         | Dai et al. (2015f)                                                |
| Selenides | <b>Ferroselite</b>  | FeSe <sub>2</sub>                                | Rare      |         |                                                                   |
| Halides   | <b>Halite</b>       | NaCl                                             | Uncommon  |         | Kalaitzidis et al. (2010), Karayigit et al. (2015)                |
| Halides   | Sylvite             | KCl                                              | Uncommon  |         | Cressey and Cressey (1988), Vassilev et al. (1994)                |
| Halides   | Bischofite          | MgCl <sub>2</sub> ·6H <sub>2</sub> O             | Rare      |         | Mackowsky (1968), Finkelman (1981)                                |
| Fluorides | Fluorite            | CaF <sub>2</sub>                                 | Rare      |         | Dai et al. (2013a)                                                |

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Table 1 (continued)

| Class      | Mineral             | Formula                                                                               | Abundance | Comment                           | Sources                                                                  |
|------------|---------------------|---------------------------------------------------------------------------------------|-----------|-----------------------------------|--------------------------------------------------------------------------|
| Oxides     | <b>Spinel</b>       |                                                                                       |           |                                   |                                                                          |
| Oxides     | <b>Chromite</b>     | MgAl <sub>2</sub> O <sub>4</sub><br>(Mg,Fe)Cr <sub>2</sub> O <sub>4</sub>             | Rare      |                                   | Alekseev (1960), Hower et al. (2018b)                                    |
| Oxides     |                     |                                                                                       | Rare      |                                   | Finkelman and Stanton (1978), Ruppert et al. (1996)                      |
| Oxides     | <b>Magnetite</b>    | FeFe <sub>2</sub> O <sub>4</sub>                                                      | Uncommon  |                                   | Pollock et al. (2000)                                                    |
| Oxides     | Corundum            | Al <sub>2</sub> O <sub>3</sub>                                                        | Rare      |                                   | Finkelman et al. (1979), Vassilev et al. (1994)                          |
| Oxides     | <b>Hematite</b>     | Fe <sub>2</sub> O <sub>3</sub>                                                        | Uncommon  |                                   | Silva et al. (2011)                                                      |
| Oxides     | <b>Ilmenite</b>     | FeTiO <sub>3</sub>                                                                    | Uncommon  |                                   | Mullai (1984), Ruppert et al. (1996), Ward et al. (1999)                 |
| Oxides     |                     |                                                                                       |           |                                   | O'Gorman (1971), Merritt (1988)                                          |
| Oxides     | <i>Cassiterite</i>  | SnO <sub>2</sub>                                                                      | Rare      |                                   |                                                                          |
| Oxides     | <b>Rutile</b>       | TiO <sub>2</sub>                                                                      | Common    |                                   | Cressey and Cressey (1988)                                               |
| Oxides     | <b>Anatase</b>      | TiO <sub>2</sub>                                                                      | Common    |                                   | Merritt (1988)                                                           |
| Oxides     | <b>Brookite</b>     | TiO <sub>2</sub>                                                                      | Uncommon  |                                   | Dai et al. (2015d, 2015f)                                                |
| Oxides     | <i>Columbite</i>    | (Fe,Mn)Nb <sub>2</sub> O <sub>6</sub>                                                 | Rare      |                                   | Finkelman (1981), Dai et al. (2015d, 2015f)                              |
| Oxides     | Brannerite          | UTi <sub>2</sub> O <sub>6</sub>                                                       | Rare      |                                   |                                                                          |
| Oxides     | <b>Uraninite</b>    | UO <sub>2</sub>                                                                       | Rare      |                                   |                                                                          |
| Hydroxide  | <b>Diaspore</b>     | α-AlO(OH)                                                                             | Uncommon  |                                   |                                                                          |
| Hydroxide  | <b>Goethite</b>     | FeO(OH)                                                                               | Uncommon  |                                   | Huggins et al. (1980), Ural and Akyildiz (2004)                          |
| Hydroxide  | <b>Gibbsite</b>     | Al(OH) <sub>3</sub>                                                                   | Uncommon  |                                   | Kalkreuth et al. (2010)                                                  |
| Hydroxide  | <b>Boehmite</b>     | γ-AlO(OH)                                                                             | Uncommon  |                                   | Ward (2002), Dai et al. (2006a)                                          |
| Hydroxide  | Lepidocrocite       | γ-FeO(OH)                                                                             | Uncommon  |                                   | Huggins et al. (1980), Kostova and Zdravkov (2007)                       |
| Hydroxide  | <i>Iserrannite</i>  | Mo <sub>2</sub> O <sub>8</sub> ·nH <sub>2</sub> O                                     | Rare      |                                   | Petrov (1963)                                                            |
| Hydroxide  | <i>Becquerelite</i> | Ca(UO <sub>2</sub> ) <sub>6</sub> O <sub>4</sub> (OH) <sub>6</sub> ·8H <sub>2</sub> O | Rare      |                                   | Akers et al. (1978)                                                      |
| Carbonates | <b>Calcite</b>      | CaCO <sub>3</sub>                                                                     | Common    |                                   |                                                                          |
| Carbonates | <b>Aragonite</b>    | CaCO <sub>3</sub>                                                                     | Uncommon  |                                   | Ward (2002)                                                              |
| Carbonates | Magnesite           | MgCO <sub>3</sub>                                                                     | Uncommon  |                                   | Brown et al. (1959), Kortenski (1992)                                    |
| Carbonates | <b>Siderite</b>     | FeCO <sub>3</sub>                                                                     | Common    |                                   |                                                                          |
| Carbonates | <b>Ankerite</b>     | Ca(Fe, Mg, Mn)(CO <sub>3</sub> ) <sub>2</sub>                                         | Common    |                                   | Dai et al. (2013b, 2018c)                                                |
| Carbonates | <b>Dolomite</b>     | CaMg(CO <sub>3</sub> ) <sub>2</sub>                                                   | Common    |                                   | Kortenski and Sotirov (2004)                                             |
| Carbonates | Strontianite        | SrCO <sub>3</sub>                                                                     | Rare      |                                   | Spencer (1910), Tarriba et al. (1995), Ward (2002)                       |
| Carbonates | <b>Witherite</b>    | BaCO <sub>3</sub>                                                                     | Uncommon  |                                   | Shoyk et al. (1992)                                                      |
| Carbonates | Alstonite           | BaCa(CO <sub>3</sub> ) <sub>2</sub>                                                   | Rare      |                                   | Cook (1976), Golab et al. (2006), Dai et al. (2008a), Zhao et al. (2014) |
| Carbonates |                     |                                                                                       |           |                                   | Dai et al. (2017)                                                        |
| Carbonates | Malachite           | Cu <sub>2</sub> CO <sub>3</sub> (OH) <sub>2</sub>                                     | Rare      |                                   |                                                                          |
| Carbonates | Dawsonite           | NaAlCO <sub>3</sub> (OH) <sub>2</sub>                                                 | Uncommon  |                                   |                                                                          |
| Carbonates |                     |                                                                                       |           |                                   |                                                                          |
| Carbonates | Bastnaesite         | (Ce,Ln)CO <sub>3</sub> F                                                              | Rare      |                                   |                                                                          |
| Nitrates   |                     |                                                                                       |           |                                   |                                                                          |
| Sulfates   | <b>Thenardite</b>   | Na <sub>2</sub> SO <sub>4</sub>                                                       | Rare      |                                   | O'Gorman and Walker (1971)                                               |
| Sulfates   | <b>Glauberite</b>   | Na <sub>2</sub> Ca(SO <sub>4</sub> ) <sub>2</sub>                                     | Rare      |                                   | Ward (2002, 2016)                                                        |
| Sulfates   | <b>Anhydrite</b>    | CaSO <sub>4</sub>                                                                     | Uncommon  |                                   | Filippidis et al. (1996), Matjie et al. (2015)                           |
| Sulfates   | <b>Barite</b>       | BaSO <sub>4</sub>                                                                     | Common    |                                   |                                                                          |
| Sulfates   | <i>Celestine</i>    | SrSO <sub>4</sub>                                                                     | Rare      | Originally described as celestite | Alekseev (1960), Dai et al. (2013b, 2014a, 2016b)                        |
| Sulfates   | <b>Alunite</b>      | KAl <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>                    | Uncommon  |                                   | Dawson et al. (2012), Ward (2016)                                        |
| Sulfates   | <b>Natroalunite</b> | (Na,K)Al <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>               | Uncommon  |                                   | Lipianski et al. (2004)                                                  |
| Sulfates   | <b>Jarosite</b>     | KFe <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>                    | common    |                                   |                                                                          |
| Sulfates   | Natrojarosite       | (Na,K)Fe <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>               | Uncommon  |                                   | Dawson et al. (2012)                                                     |
| Sulfates   | <b>Kieserite</b>    | MgSO <sub>4</sub> ·H <sub>2</sub> O                                                   | rare      |                                   | Mackowsky (1968), Ward (1991)                                            |
| Sulfates   | <b>Szomolnokite</b> | FeSO <sub>4</sub> ·H <sub>2</sub> O                                                   | Uncommon  |                                   | Rao and Gluskoter (1973), Oliveira et al. (2012), Dai et al. (2013b)     |

(continued on next page)

Table 1 (continued)

| Class      | Mineral              | Formula                                                                                                 | Abundance | Comment | Sources                                                                                        |
|------------|----------------------|---------------------------------------------------------------------------------------------------------|-----------|---------|------------------------------------------------------------------------------------------------|
| Sulfates   | <b>Rozenite</b>      | FeSO <sub>4</sub> ·4H <sub>2</sub> O                                                                    | Uncommon  |         | Querol et al. (1991)                                                                           |
| Sulfates   | <i>Siderotil</i>     | FeSO <sub>4</sub> ·5H <sub>2</sub> O                                                                    | rare      |         | Finkelman et al. (1979), Li et al. (2016a)                                                     |
| Sulfates   | <b>Hexahydrite</b>   | MgSO <sub>4</sub> ·6H <sub>2</sub> O                                                                    | Uncommon  |         | Foscolos et al. (1989), Ward (1991, 1992)                                                      |
| Sulfates   | <b>Melanterite</b>   | FeSO <sub>4</sub> ·7H <sub>2</sub> O                                                                    | Uncommon  |         | Rao and Gluskoter (1973), Oliveira et al. (2012)                                               |
| Sulfates   | <b>Epsomite</b>      | MgSO <sub>4</sub> ·7H <sub>2</sub> O                                                                    | Uncommon  |         | Querol et al. (1991), Ward (1992), López-Buendía et al. (2007)                                 |
| Sulfates   | <b>Alunogen</b>      | Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·17H <sub>2</sub> O                                     | Uncommon  |         | Frazier and Belcher (1973), Miller et al. (1979), Ward et al. (2001b)                          |
| Sulfates   | <b>Coquimbite</b>    | Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·9H <sub>2</sub> O                                      | Uncommon  |         | Rao and Gluskoter (1973), Oliveira et al. (2012)                                               |
| Sulfates   | <i>Romerite</i>      | FeFe <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub> ·12H <sub>2</sub> O                                   | Rare      |         | Gluskoter (1975)                                                                               |
| Sulfates   | <i>Halotrichite</i>  | FeAl <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub> ·22H <sub>2</sub> O                                   | Uncommon  |         | Shaver et al. (2006)                                                                           |
| Sulfates   | <b>Pickeringite</b>  | MgAl <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub> ·22H <sub>2</sub> O                                   | Uncommon  |         | Cobb et al. (1979), Ward (2016)                                                                |
| Sulfates   | Al-rich pickeringite |                                                                                                         | Uncommon  |         | Cobb et al. (1979)                                                                             |
| Sulfates   | <i>Kalinite</i>      | KAl(SO <sub>4</sub> ) <sub>2</sub> ·11H <sub>2</sub> O                                                  | Uncommon  |         |                                                                                                |
| Sulfates   | <i>Alum-(K)</i>      | KAl(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O                                                  | Uncommon  |         | Stutzer (1940)                                                                                 |
| Sulfates   | <b>Tschermigite</b>  | NH <sub>4</sub> Al(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O                                   | Uncommon  |         | Foscolos et al. (1989), Ward (1991, 1992)                                                      |
| Sulfates   | <b>Blödite</b>       | Na <sub>2</sub> Mg(SO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O                                    | Uncommon  |         | Yossifova (2007, 2014)                                                                         |
| Sulfates   | <i>Mirabilite</i>    | Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O                                                     | Uncommon  |         | Mackowsky (1968), López-Buendía et al. (2007)                                                  |
| Sulfates   | <b>Gypsum</b>        | CaSO <sub>4</sub> ·2H <sub>2</sub> O                                                                    | common    |         |                                                                                                |
| Sulfates   | <b>Bassanite</b>     | CaSO <sub>4</sub> ·0.5H <sub>2</sub> O                                                                  | Common    |         |                                                                                                |
| Sulfates   | <b>Copiapite</b>     | FeFe <sub>2</sub> (SO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub> ·20H <sub>2</sub> O                 | Uncommon  |         | Querol et al. (1991)                                                                           |
| Sulfates   | Aluminite            | Al <sub>2</sub> SO <sub>4</sub> (OH) <sub>4</sub> ·7H <sub>2</sub> O                                    | Uncommon  |         | Ward et al. (2001b), Cutruneo et al. (2014)                                                    |
| Sulfates   | Sideronatrite        | Na <sub>2</sub> Fe(SO <sub>4</sub> ) <sub>2</sub> (OH)·3H <sub>2</sub> O                                | Uncommon  |         |                                                                                                |
| Chromates  | <b>Crocoite</b>      | PbCrO <sub>4</sub>                                                                                      | Uncommon  |         | Li et al. (2001)                                                                               |
| Phosphates | <b>Xenotime</b>      | YPO <sub>4</sub>                                                                                        | Uncommon  |         | Finkelman and Stanton (1978), Dai et al., 2016a)                                               |
| Phosphates | <b>Monazite</b>      | CePO <sub>4</sub>                                                                                       | Uncommon  |         | Hower et al. (1999), Dai et al. (2014a, 2015a)                                                 |
| Phosphates | <b>Crandallite</b>   | CaAl <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>5</sub> ·H <sub>2</sub> O                   | Uncommon  |         | Cressey and Cressey (1988), Ward et al. (1996), Rao and Walsh (1997, 1999), Dai et al. (2015a) |
| Phosphates | <b>Goyazite</b>      | SrAl <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>5</sub> ·H <sub>2</sub> O                   | Uncommon  |         | Cressey and Cressey (1988), Ward et al. (1996), Rao and Walsh (1997, 1999), Dai et al. (2015a) |
| Phosphates | <b>Gorceixite</b>    | BaAl <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>5</sub> ·H <sub>2</sub> O                   | Uncommon  |         | Cressey and Cressey (1988), Ward et al. (1996), Rao and Walsh (1997, 1999), Dai et al. (2015a) |
| Phosphates | <b>Florencite</b>    | CeAl <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>                                     | Uncommon  |         | Cressey and Cressey (1988), Ward et al. (1996), Rao and Walsh (1997, 1999), Dai et al. (2015a) |
| Phosphates | <b>Apatite</b>       | Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> (F,Cl,OH)                                               | Common    |         | Cressey and Cressey (1988), Ward et al. (1996), Rao and Walsh (1997, 1999), Dai et al. (2015a) |
| Phosphates | <b>Vivianite</b>     | Fe <sub>3</sub> <sup>2+</sup> (PO <sub>4</sub> ) <sub>2</sub> ·8H <sub>2</sub> O                        | Rare      |         | Akers et al. (1978), Ward et al. (1996)                                                        |
| Phosphates | <i>Messelite</i>     | Ca <sub>2</sub> (Fe <sup>2+</sup> , Mn <sup>2+</sup> )(PO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O | Rare      |         | Vertushkov (1953)                                                                              |
| Phosphates | <b>Rhabdophane</b>   | Ce(PO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O                                                     | Uncommon  |         | Dai et al. (2014b, 2015a)                                                                      |
| Phosphates | <i>Autunite</i>      | Ca(UO <sub>2</sub> ) <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> ·10-12H <sub>2</sub> O                | Rare      |         | Akers et al. (1978)                                                                            |
| Phosphates | <i>Meta-autunite</i> | Ca(UO <sub>2</sub> ) <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> ·2-6H <sub>2</sub> O                  | Rare      |         | Akers et al. (1978)                                                                            |

(continued on next page)

Table 1 (continued)

| Class                   | Mineral                      | Formula                                                                                                                                                                                                                                                                                                                                                    | Abundance | Comment                              | Sources                                                                   |
|-------------------------|------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------|--------------------------------------|---------------------------------------------------------------------------|
| Phosphates              | <i>Chernikovite</i>          | $(\text{H}_3\text{O})(\text{UO}_2)(\text{PO}_4)_3 \cdot 3\text{H}_2\text{O}$                                                                                                                                                                                                                                                                               | Rare      | Originally described as H-autinite   | Akers et al. (1978)                                                       |
| Phosphates              | <i>Na-Autinite</i>           | $\text{Na}_2(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$                                                                                                                                                                                                                                                                                      | Rare      |                                      | Akers et al. (1978)                                                       |
| Phosphates              | <i>Metauranacrite</i>        | $\text{Ba}(\text{UO}_2)(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$                                                                                                                                                                                                                                                                                          | Rare      |                                      | Akers et al. (1978)                                                       |
| Phosphates              | <i>Torbernite</i>            | $\text{Cu}(\text{UO}_2)(\text{PO}_4)_2 \cdot 12\text{H}_2\text{O}$                                                                                                                                                                                                                                                                                         | Rare      |                                      | Velichkov (2012)                                                          |
| Phosphates              | <i>Saleeite</i>              | $\text{Mg}(\text{UO}_2)(\text{PO}_4)_2 \cdot 10\text{H}_2\text{O}$                                                                                                                                                                                                                                                                                         | Rare      |                                      | Akers et al. (1978)                                                       |
| Phosphates              | <i>Metatorbernite</i>        | $\text{Cu}(\text{UO}_2)(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$                                                                                                                                                                                                                                                                                          | Rare      |                                      | Akers et al. (1978)                                                       |
| Phosphates              | <i>Sabugalite</i>            | $\text{HAl}(\text{UO}_2)_4(\text{PO}_4)_4 \cdot 16\text{H}_2\text{O}$                                                                                                                                                                                                                                                                                      | Rare      |                                      | Akers et al. (1978)                                                       |
| Arsenates               | <i>Zeunerite</i>             | $\text{Cu}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 10\text{--}16\text{H}_2\text{O}$                                                                                                                                                                                                                                                                           | Rare      |                                      | Akers et al. (1978), Eskenazy and Velichkov (2012)                        |
| Arsenates               | <i>Abernathyite</i>          | $\text{K}(\text{UO}_2)(\text{AsO}_4) \cdot 3\text{H}_2\text{O}$                                                                                                                                                                                                                                                                                            | Rare      |                                      | Akers et al. (1978)                                                       |
| Vanadates               | <i>Carnotite</i>             | $\text{K}_2(\text{UO}_2)(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}$                                                                                                                                                                                                                                                                                         | Rare      |                                      | Akers et al. (1978), Papanicolaou et al. (2004), Dai and Finkelman (2018) |
| Silicates               |                              |                                                                                                                                                                                                                                                                                                                                                            |           |                                      |                                                                           |
| Nesosilicate            | <i>Olivine</i>               | $(\text{Mg}, \text{Fe})_2\text{SiO}_4$                                                                                                                                                                                                                                                                                                                     | Rare      |                                      | Erkoyun et al. (2017), This study                                         |
| Nesosilicate            | <i>Zircon</i>                | $\text{ZrSiO}_4$                                                                                                                                                                                                                                                                                                                                           | Common    |                                      |                                                                           |
| Nesosilicate            | <i>Coffinite</i>             | $\text{U}(\text{SiO}_4)_{1-x}(\text{OH})_{4x}$                                                                                                                                                                                                                                                                                                             | Rare      |                                      | Akers et al. (1978), Dai et al. (2015f)                                   |
| Nesosilicate            | <b>Titanite</b>              | $\text{CaTiSiO}_4(\text{O}, \text{OH}, \text{F})$                                                                                                                                                                                                                                                                                                          | Rare      | Originally described as sphene       | Finkelman and Stanton (1978), Sutcu and Karayigit (2015)                  |
| Nesosilicate            | Garnet                       | $(\text{Mg}, \text{Fe}, \text{Mn}, \text{Ca})_3(\text{Al}, \text{Fe}, \text{Ti}, \text{Cr})\text{Si}_5\text{O}_{12}$                                                                                                                                                                                                                                       | Uncommon  |                                      | Spears and Arbuzov (2019)                                                 |
| Nesosilicate            | Grossular                    | $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$                                                                                                                                                                                                                                                                                                           | Rare      | Originally described as grossularite | Mitra (1954), Wang et al. (2012)                                          |
| Nesosilicate            | Mullite                      | $\text{Al}_2\text{xSi}_{2-2x}\text{O}_{10-x}$                                                                                                                                                                                                                                                                                                              | Rare      |                                      | Marshall (1959), Golab and Carr (2004)                                    |
| Nesosilicate            | <i>Andalusite</i>            | $\text{Al}_2(\text{SiO}_3)_2\text{O}$                                                                                                                                                                                                                                                                                                                      | Rare      |                                      |                                                                           |
| Nesosilicate            | Kyanite                      | $\text{Al}_2(\text{SiO}_3)_2\text{O}$                                                                                                                                                                                                                                                                                                                      | Rare      |                                      | Akers et al. (1978)                                                       |
| Nesosilicate            | <i>Uranophane</i>            | $\text{Ca}(\text{UO}_2)_2\text{SiO}_3(\text{OH})_2 \cdot 5\text{H}_2\text{O}$                                                                                                                                                                                                                                                                              | Rare      |                                      | Nelson (1953)                                                             |
| Nesosilicate            | Staurolite                   | $(\text{Fe}, \text{Mg}, \text{Zn})_2(\text{Al}, \text{Fe}, \text{Ti})_9\text{O}_6 \cdot (\text{Si}, \text{Al})\text{O}_4(\text{O}, \text{OH})_4$                                                                                                                                                                                                           | Rare      |                                      | Kortenski and Sotirov (2000)                                              |
| Nesosilicate            | Topaz                        | $\text{Al}_2\text{SiO}_4(\text{OH}, \text{F})_2$                                                                                                                                                                                                                                                                                                           | Rare      |                                      | Finkelman and Stanton (1978)                                              |
| Sorosilicate            | Epidote                      | $\text{Ca}_2\text{Al}_2\text{O}(\text{Al}, \text{Fe}, \text{Mn}, \text{OH})[\text{Si}_2\text{O}_7]/\text{SiO}_4$                                                                                                                                                                                                                                           | Uncommon  |                                      |                                                                           |
| Sorosilicate            | <i>Allanite</i>              | $(\text{Ca}, \text{Mn}, \text{Ce}, \text{La}, \text{Y}, \text{Th})_2(\text{Fe}^{2+}, \text{Fe}^{3+}, \text{Ti})(\text{Al}, \text{Fe}^{3+})_2\text{O}_3\text{OH}$<br>[ $\text{Si}_2\text{O}_7$ ]/ $[\text{SiO}_4]$                                                                                                                                          | Rare      |                                      |                                                                           |
| Cyclosilicate           | <b>Tourmaline</b>            | (Na, Ca)<br>$(\text{Mg}, \text{Fe}, \text{Mn}, \text{Li}, \text{Al})_3(\text{Al}, \text{Mg}, \text{Fe}^{3+})_6[\text{Si}_6\text{O}_{18}]_3\text{BO}_3 \cdot 3(\text{O}, \text{O}-\text{H})_3(\text{OH}, \text{F})$<br>$(\text{Ca}, \text{Na}, \text{Li})(\text{Mg}, \text{Fe}^{2+}, \text{Fe}^{3+}, \text{Mn}, \text{Cr}, \text{Al})\text{Si}_5\text{O}_6$ | Uncommon  |                                      | Queroi et al. (1996), Boyd (2002)                                         |
| Inosilicate             | Pyroxene                     | $\text{CaMgSi}_2\text{O}_6$                                                                                                                                                                                                                                                                                                                                | Uncommon  |                                      | Brownfield et al. (1995)                                                  |
| Inosilicate             | Diopside                     | $(\text{Ca}, \text{Mg}, \text{Fe}^{2+}, \text{Al})\text{Si}_2\text{O}_6$                                                                                                                                                                                                                                                                                   | Rare      |                                      | Finkelman and Stanton (1978)                                              |
| Inosilicate             | Augite                       | $(\text{Na}, \text{K}, \text{Ca})(\text{Na}, \text{Mg}, \text{Fe}^{2+}, \text{Mn}^{2+}, \text{Ca})_2(\text{Na}, \text{Mg}, \text{Fe}^{2+}, \text{Mn}^{2+}, \text{Al}, \text{Fe}^{3+}, \text{Cr}^{3+}, \text{Mn}^{3+}, \text{Ti})_5(\text{Si}, \text{Al}, \text{Ti})_8\text{O}_{22}$<br>(OH, F, Cl, O) <sub>2</sub>                                         | Uncommon  |                                      | Kortenski and Sotirov (2002), Grigore and Sakurovs (2016)                 |
| Inosilicate             | <b>Amphibole</b>             | $\text{Ca}_2(\text{Mg}, \text{Fe}^{2+})_4\text{Al}(\text{Si}, \text{AlO}_{22})(\text{OH}, \text{F})_2$                                                                                                                                                                                                                                                     | Uncommon  |                                      | Yossifova et al. (2011)                                                   |
| Inosilicate             | <b>Hornblende</b>            | $(\text{Na}, \text{K})(\text{Na}_2\text{Mg}, \text{Fe}^{3+}, \text{Si}_6\text{O}_{22})(\text{OH})_2$                                                                                                                                                                                                                                                       | Rare      |                                      | Francis (1961), Brownfield et al. (1995), Erik and Sancar (2010)          |
| Inosilicate             | <i>Magnesioarphvedsonite</i> | $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$                                                                                                                                                                                                                                                                                                    | Rare      |                                      | Finkelman and Stanton (1978)                                              |
| Phyllosilicate-Mica     | <b>Muscovite</b>             | $\text{NaAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$                                                                                                                                                                                                                                                                                                   | Uncommon  |                                      | Dai et al. (2018b)                                                        |
| Phyllosilicate-Mica     | <b>Paragonite</b>            | $\text{KV}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$                                                                                                                                                                                                                                                                                                     | Uncommon  |                                      | Susilawati and Ward (2006), Permana et al. (2013)                         |
| Phyllosilicate-Mica     | Roscoelite                   | $\text{KMg}(\text{Fe}^{2+})_3(\text{Al}, \text{Fe}^{3+})\text{Si}_3\text{O}_{10}(\text{OH}, \text{F})_2$                                                                                                                                                                                                                                                   | Rare      |                                      | Dai et al. (2017)                                                         |
| Phyllosilicate-Mica     | <b>Biotite</b>               | $\text{Mg}_6(\text{Si}_8\text{O}_{20})(\text{OH})_4$                                                                                                                                                                                                                                                                                                       | Uncommon  |                                      | Erkoyun et al. (2019)                                                     |
| Phyllosilicate-Mica     | <i>Talc</i>                  | $\text{Al}_2(\text{Si}_4\text{O}_{10})(\text{OH})_4$                                                                                                                                                                                                                                                                                                       | Rare      |                                      | Finkelman and Stanton (1978)                                              |
| Phyllosilicate-Chlorite | <b>Pyrophyllite</b>          | $(\text{Mg}, \text{Fe}^{2+}, \text{Fe}^{3+}, \text{Mn}, \text{Ni}, \text{Na}, \text{Li}, \text{Al})_6(\text{Si}, \text{Al})_4\text{O}_{10}[(\text{OH})_8]$                                                                                                                                                                                                 | Uncommon  |                                      | Dai et al. (2018b)                                                        |
| Phyllosilicate-Chlorite | <b>Chlorite</b>              |                                                                                                                                                                                                                                                                                                                                                            | Uncommon  |                                      | Dai and Chou (2007), Dai et al. (2018b)                                   |

(continued on next page)

Table 1 (continued)

| Class                         | Mineral               | Formula                                                                                                                                                          | Abundance | Comment                                                                                     | Sources                                                                     |
|-------------------------------|-----------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------|---------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------|
| Phyllosilicate-Chlorite       | Chamosite             | $\text{Fe}_2^{2+}(\text{Fe}_4^{2+}, \text{Al}_2)[\text{Si}_6, \text{Al}_2]\text{O}_{20}(\text{OH})_{16}$                                                         | Uncommon  | Also includes material previously identified as thuringite (no longer a valid mineral name) | Dai and Chou (2007)                                                         |
| Phyllosilicate-Chlorite       | Cookeite              | $\text{Al}_4(\text{Li}_{12}, \text{Al}_{12})[\text{Si}_{16}, \text{Al}_2]\text{O}_{20}(\text{OH})_{16}$                                                          | Uncommon  |                                                                                             | Zhao et al. (2018)                                                          |
| Phyllosilicate-Chlorite       | Pennantite            | $\text{Mn}_6^{2+}(\text{Mn}_4^{2+}, \text{Al}_2)[\text{Si}_6, \text{Al}_2]\text{O}_{20}(\text{OH})_{16}$                                                         | Rare      |                                                                                             |                                                                             |
| Phyllosilicate-Chlorite       | Clinocllore           | $\text{Mg}_5\text{Al}(\text{AlSi}_3\text{O}_{10})(\text{OH})_8$                                                                                                  | Uncommon  | Originally identified as prochlorite (no longer a valid mineral name)                       | Montross et al. (2018)                                                      |
| Phyllosilicate                | <i>Chrysotile</i>     | $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$                                                                                                                  | Rare      |                                                                                             | Rekus and Haberkorn III (1966), Brownfield et al. (1995)                    |
| Phyllosilicate-Clay           | <b>Kaolinite</b>      | $\text{Al}_2[\text{Si}_2\text{O}_5](\text{OH})_4$                                                                                                                | Common    |                                                                                             | Nalwalk et al. (1974), Permana et al. (2013), Zhao et al. (2018)            |
| Phyllosilicate-Clay           | <b>Dickite</b>        | $\text{Al}_2[\text{Si}_2\text{O}_5](\text{OH})_4$                                                                                                                | Uncommon  |                                                                                             | Nalwalk et al. (1974), Permana et al. (2013)                                |
| Phyllosilicate-Clay           | Nacrite               | $\text{Al}_2[\text{Si}_2\text{O}_5](\text{OH})_4$                                                                                                                | Rare      |                                                                                             | Ward and Roberts (1990)                                                     |
| Phyllosilicate-Clay           | Halloysite            | $\text{Al}_2[\text{Si}_2\text{O}_5](\text{OH})_4 \cdot 2\text{H}_2\text{O}$                                                                                      | Uncommon  |                                                                                             |                                                                             |
| Phyllosilicate-Clay           | Metahalloysite        | $\text{Al}_2[\text{Si}_2\text{O}_5](\text{OH})_4$                                                                                                                | Rare      |                                                                                             |                                                                             |
| Phyllosilicate-Clay           | <i>Allophane</i>      | $(\text{Al}_2\text{O}_3)(\text{SiO}_2)_{1.3-2.5} \cdot 2.5-3\text{H}_2\text{O}$                                                                                  | Rare      |                                                                                             | Deul (1959), Sudo et al. (1981)                                             |
| Phyllosilicate-Clay           | <b>Illite</b>         | $\text{K}_{0.65}(\text{Al}, \text{Fe}, \text{Mg})_{2.0}[\text{Al}_{0.65}, \text{Si}_{1.35}]\text{O}_{10}(\text{OH})_2$                                           | Common    | Includes hydromuscovite and hydromica as these are no longer valid names                    |                                                                             |
| Phyllosilicate-Clay           | <i>Glauconite</i>     | $\text{K}_{0.8}\text{R}_{1.33}^{3+}\text{R}_{0.67}^{2+}(\text{Al}_{0.13}, \text{Si}_{1.87})\text{O}_{10}(\text{OH})_2$                                           | Rare      |                                                                                             | Falcon (1978)                                                               |
| Phyllosilicate-Clay           | <i>Brammhallite</i>   | $\text{Na}_{0.65}\text{Al}_2(\text{Al}_{0.65}, \text{Si}_{1.35})\text{O}_{10}(\text{OH})_2$                                                                      | Rare      |                                                                                             | Foster and Feicht (1946)                                                    |
| Phyllosilicate-Clay           | <b>Tobelite</b>       | $\text{NH}_4\text{Al}_2(\text{AlSi}_3\text{O}_{10})\text{OH}_2$                                                                                                  | Uncommon  |                                                                                             | Daniels and Altaner (1993), Dai et al. (2012c, 2017), Permana et al. (2013) |
| Phyllosilicate-Clay           | <b>Smectite</b>       | $\text{M}_x(\text{Si}_4)(\text{Al}_{2-x})(\text{Mg}, \text{Fe}^{3+})_2\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$                                      | Uncommon  |                                                                                             | Zhao et al. (2012a, 2012b)                                                  |
| Phyllosilicate-Clay           | Montmorillonite       | $\text{M}_x(\text{Si}_{4-x}\text{Al}_x)(\text{Al}_{2-x}\text{Mg}_x)\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$                                         | Uncommon  |                                                                                             | Zhao et al. (2012a, 2012b)                                                  |
| Phyllosilicate-Clay           | Beidellite            | $\text{M}_x(\text{Si}_{4-x}\text{Al}_x)(\text{Al}_2\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O})$                                                        | Rare      |                                                                                             | Erkoyun et al. (2017)                                                       |
| Phyllosilicate-Clay           | <i>Nontronite</i>     | $\text{M}_x(\text{Si}_{4-x}\text{Al}_x)(\text{Fe}_2^{3+})\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$                                                   | Rare      |                                                                                             | Ruppert et al. (1996), Liu et al. (2019)                                    |
| Phyllosilicate-Clay           | <i>Vermiculite</i>    | $\text{Mg}_2(\text{H}_2\text{O})_n[(\text{Si}, \text{Al})_4(\text{Mg}, \text{Al}, \text{Fe})_3\text{O}_{10}](\text{OH})_2$                                       | Rare      |                                                                                             | Valentim et al. (2016)                                                      |
| Tectosilicate silica minerals | <b>Quartz</b>         | $\text{SiO}_2$                                                                                                                                                   | Common    |                                                                                             |                                                                             |
| Tectosilicate silica minerals | <b>Opal</b>           | $\text{SiO}_2 \cdot n\text{H}_2\text{O}$                                                                                                                         | Uncommon  |                                                                                             | Querol et al. (1999)                                                        |
| Tectosilicate silica minerals | <b>Chalcedony</b>     | $\text{SiO}_2$                                                                                                                                                   | Uncommon  |                                                                                             | Burger et al. (1990)                                                        |
| Tectosilicate feldspars       | <b>Microcline</b>     | $\text{KAlSi}_3\text{O}_8$                                                                                                                                       | Uncommon  |                                                                                             | Querol et al. (1997a)                                                       |
| Tectosilicate feldspars       | <b>Orthoclase</b>     | $\text{KAlSi}_3\text{O}_8$                                                                                                                                       | Uncommon  |                                                                                             | Golab and Carr (2004)                                                       |
| Tectosilicate feldspars       | <b>Sanidine</b>       | $(\text{Na}, \text{K})\text{AlSi}_3\text{O}_8$                                                                                                                   | Uncommon  |                                                                                             | Dai et al. (2008a, 2018a)                                                   |
| Tectosilicate feldspars       | <b>Plagioclase</b>    | $\text{NaAlSi}_3\text{O}_8$                                                                                                                                      | Uncommon  |                                                                                             | Zhao et al. (2012a), Dai et al. (2018a)                                     |
| Tectosilicate feldspars       | <b>Anorthite</b>      | $\text{CaAl}_2\text{Si}_2\text{O}_8$                                                                                                                             | Uncommon  |                                                                                             | Kortenski and Sotirov (2000)                                                |
| Tectosilicate feldspars       | <b>Albite</b>         | $\text{NaAlSi}_3\text{O}_8$                                                                                                                                      | Uncommon  |                                                                                             | Dai et al. (2013b, 2018a, 2018c)                                            |
| Tectosilicate feldspars       | <b>Buddingtonite</b>  | $\text{NH}_4\text{AlSi}_3\text{O}_8$                                                                                                                             | Uncommon  |                                                                                             | Dai et al. (2018c)                                                          |
| Tectosilicate-zeolite         | <b>Analcime</b>       | $\text{Na}[\text{AlSi}_2\text{O}_6] \cdot \text{H}_2\text{O}$                                                                                                    | Rare      |                                                                                             | Rao (1977), Finkelman (1988), Wang et al. (2018)                            |
| Tectosilicate-zeolite         | <b>Heulandite</b>     | $(\text{Ca}_{0.5}, \text{Sr}_{0.5}, \text{Ba}_{0.5}, \text{Mg}_{0.5}, \text{Na}, \text{K})_9[\text{Al}_9\text{Si}_{27}\text{O}_{72}] \cdot 24\text{H}_2\text{O}$ | Rare      |                                                                                             | Querol et al. (1997b)                                                       |
| Tectosilicate-zeolite         | <b>Clinoptilolite</b> | $(\text{Na}, \text{K}, \text{Ca}_{0.5}, \text{Sr}_{0.5}, \text{Ba}_{0.5}, \text{Mg}_{0.5})_6[\text{Al}_6\text{Si}_{30}\text{O}_{72}] \cdot 22\text{H}_2\text{O}$ | Rare      |                                                                                             | Querol et al. (1997b) and Pollock et al. (2000)                             |
| Tectosilicate-zeolite         | <i>Laumontite</i>     | $\text{Ca}_4[\text{Al}_5\text{Si}_{14}\text{O}_{48}] \cdot 18\text{H}_2\text{O}$                                                                                 | Rare      |                                                                                             | Cook (1976)                                                                 |
| Tectosilicate-zeolite         | Lawsonite             | $\text{CaAl}_2(\text{Si}_2\text{O}_7)(\text{OH})_2 \cdot \text{H}_2\text{O}$                                                                                     | Rare      |                                                                                             | Sarofim et al. (1977)                                                       |
| Organic                       | <b>Weddellite</b>     | $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$                                                                                                               | Rare      |                                                                                             | Ward (1974), Dai et al. (2015c)                                             |
| Organic                       | <b>Whewellite</b>     | $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$                                                                                                                | Rare      |                                                                                             | Ward (1974), Dai et al. (2015c)                                             |
| Organic                       | <i>Mellite</i>        | $\text{Al}_2(\text{C}_6(\text{COO})_6) \cdot 16\text{H}_2\text{O}$                                                                                               | Rare      |                                                                                             | Goldschmidt (1954)                                                          |
| Amorphous/mixtures            | Melnikovite           | $\text{FeS}_2$                                                                                                                                                   | Uncommon  | Amorphous equivalent of pyrite                                                              | Çelik et al. (2017)                                                         |
| Amorphous/mixtures            | <i>Jordisite</i>      | $\text{MoS}_2$                                                                                                                                                   | Rare      | Amorphous equivalent of molybdenite                                                         | Petrov (1963)                                                               |
| Amorphous/mixtures            | <i>Collophane</i>     | $\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{CO}_3)$                                                                                                              | Uncommon  | Amorphous equivalent of apatite                                                             | Mackowsky (1968), Ward (1992), Ward et al. (1996)                           |
| Amorphous/mixtures            | Pitchblende           |                                                                                                                                                                  | Rare      | Mixed uranium oxides. Not a valid mineral species                                           | Dai et al. (2015a, 2015b)                                                   |

(continued on next page)

Table 1 (continued)

| Class              | Mineral           | Formula | Abundance | Comment                                                 | Sources                       |
|--------------------|-------------------|---------|-----------|---------------------------------------------------------|-------------------------------|
| Amorphous/mixtures | <i>Leucoxene</i>  |         | Uncommon  | Mixed iron-titanium oxides. Not a valid mineral species |                               |
| Amorphous/mixtures | <i>Limonite</i>   |         | Uncommon  | Mixed iron oxy-hydroxides. Not a valid mineral species  | Swaine (1990)                 |
| Amorphous/mixtures | <i>Dopplerite</i> |         | Rare      | Amorphous Ca bearing organic resin.                     | Lissner (1956), Wagner (1982) |
| Amorphous/mixtures | <i>Sericite</i>   |         | Rare      | A descriptive term applied to fine-grained white mica.  | Kortenski and Sotirov (2000)  |

U-bearing minerals from Akers et al. (1978); King and Young (1956), and White (1958); otherwise as indicated.

coal and in the mineral hosts (e.g., Spears and Zheng, 1999; Zhao et al., 2019) based on correlations between the concentration of individual major and trace elements in a series of related coal samples. Some authors have pointed out the cautions using statistical analyses for associations between minerals (or ash yield) and elements (e.g., Mraw et al., 1983; Glick and Davis, 1987). Eskanazy et al. (2010) has shown that there are potential problems with this approach if the sample suite contains a wide range of ash yields. Geboy et al. (2013) proposed a mathematical approach to keep consistent interpretations of whole-coal versus ash basis in coal geochemistry. Ward (2016) showed that this approach may be more effective if the nature and quantitative content of the different minerals in coal samples have been independently established (e.g., by XRD analysis on low-temperature ashes of coal), and this would allow the trace element concentrations to be related more directly to particular minerals in coal. The effectiveness of this integrated approach has been verified by a number of studies (e.g., Ward et al., 1999; Dai et al., 2012a, 2015a, 2015b; Zhao et al., 2019).

Some 200 minerals have been observed in coal. Finkelman (1981) contains a list of about 175 minerals that had been reported from coal, and, many more have been recorded in the intervening 40 years. Some of these more recently reported minerals are included by Ward (2016) in a comprehensive list of minerals in coal. Table 1 borrows mainly from these two references, augmented by other recent reports on minerals found in coal. The modes of occurrence and origins of most of these minerals have been comprehensively reviewed by Ward (2002, 2016).

The minerals identified in coal and LTAs (low-temperature ashes) of coal can be classified as silicate, sulfides, carbonate, oxides and hydroxides, selenides, phosphates and oxalates, based on their elemental compositions and crystal structures; and as common, uncommon, and rare, on the basis of their abundance in worldwide samples. We acknowledge that there are questionable or suspect identifications for some minerals, particularly for those that are rare in coal. Due to limitations of each method, for several minerals, many studies, including this investigation, are constrained to use the generic terms such as 'clays', 'silicates', and 'carbonates'.

In reality, some of the minerals on the current list have not been verified and should be considered as speculative until conformation is forthcoming. The table will be posted on the website of The Society for Organic Petrology (TSOP) and updated periodically. The authors welcome all comments and inputs on the table and anyone wishing to add a new mineral along with supporting evidence, or verified evidence for the minerals that have not been verified in the Table 1, could submit their mineral materials through the entry [www.tsop.org](http://www.tsop.org).

### 3. Minerals and mineral groups as host of chemical elements

#### 3.1. Silicates as hosts of chemical elements

The silicates are the largest, most complex, and generally the most abundant group of minerals in coal (Table 1). Not surprisingly the silicates are the hosts of many elements found in coal, particularly of major elements including Si and Al, and to a lesser extent, K, Ca, Na, Mg, and Fe. The silicates include the clay minerals, the most diverse and generally most abundant mineral group in coal, and quartz, perhaps the most common mineral in coal. Other important silicates are micas, analcime (Finkelman, 1988; Wang et al., 2018), and various feldspars.

Of course Si and Al (90%/65%: percentages are the proportion of the element associated with the mineral group in a suite of 14 bituminous coals and six low-rank coals, respectively, as determined by Finkelman et al., 2018) are essential components of the clays. In addition, based on data of leaching coals with hydrofluoric acid, Finkelman et al. (2018) showed that Sb (25%/50%), Be (60%/30%), Cs (100%/80%), Cr (75%/75%), Li (90%/70%), Mo (30%/65%), K (95%/75%), Rb (90%/85%), Sc (90%/95%), Na (80%/ < 35%), Ti (65%/70%), and V (65%/50%) are associated with silicates, most likely the

clays. There was no leaching data available for Ga, which is assumed to also be largely associated with the clays (Finkelman, 1981), and in some cases, with boehmite and goyazite (Ward, 2002, 2016; Dai et al., 2006a, 2012a).

Other elements with silicate mineral associations include Ba (40–60%/10%); Ni (30%/20%); Sr (25%/0); Ta (25%/40%); U (25%, 35%); the rare earth elements (REE, 20%/50–60%), Zr (70%/70%) and Hf (70%/70%) in zircons; and Ge most likely associated with quartz (Finkelman et al., 2018).

It is highly likely that the clays, relative to other silicates, are the primary hosts of major, and, in particular, a substantial number of trace elements in coal. For example, quartz, chalcedony, and cristobalite in coal tends to be low in most elements with exceptions of Si, O and possibly Li. Zircon and tourmaline have been found in some coals and are hosts of a limited number of trace elements, e.g., Zr, Hf, REE, Nb, Ta, Th, and U (Zircon); and Li, B, and F (tourmaline). A number of studies have shown strong correlations between of many trace elements and clay minerals (e.g., Finkelman, 1981). This is because clays, usually negatively charged in nature, have high surface to volume ratio, which enable trace elements, usually positively charged, to be adsorbed on its surface. Also, some clays have interlayer space, where cation exchange may take place. Kuhn et al. (1980) showed that at least 20 trace elements are associated with clay minerals based on the investigation of 27 coals from eight areas in USA. Some studies have shown that some elements, usually occurring at a low concentration level in coal and as adsorbed forms, could be the major component of clay minerals. For example, Li-bearing minerals, cookeite  $[(\text{Al}_2\text{Li})\text{Al}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_8]$ , has been identified in an anthracite in the Jincheng deposit in China, and was derived from the reaction of previously-formed kaolinite with Li ions (Zhao et al., 2018). In the Guanbanwusu Al-Ga-REY coal-hosted deposit in China, chlorite phase has a composition intermediate between chamosite and a Li-bearing cookeite component (Dai et al., 2012a). Another such case is V-bearing mineral, roscoelite,  $\text{K}(\text{V}^{3+}, \text{Al})_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$ , has been identified in a late Permian coal in the Moxinpo Coalfield in southwestern China (Dai et al., 2017).

Carbon, H, O, and S, which usually occur in organic compounds in coal, in many cases are mineral crystal structure components. For example, nitrogen as  $\text{NH}_4^+$  forms has been found in several minerals, such as tobelite  $[(\text{NH}_4, \text{K})\text{Al}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2]$  (including ammonian illite) (Dai et al., 2012c, 2017; Ward, 2002, 2016), buddingtonite  $[(\text{NH}_4)(\text{AlSi}_3)\text{O}_8]$  (Dai et al., 2018c), and to a lesser extent, tschermigite  $[\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}]$ . In addition to tschermigite, which may be found in the LTA residues produced from some coals, particularly lower-rank materials (e.g. Foscolos et al., 1989; Ward, 1991, 1992, 2002, 2016), these  $\text{NH}_4^+$ -bearing minerals, as well as pyrophyllite  $[\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2]$ , chlorite, cookeite, roscoelite and paragonite (or brammallite;  $\text{NaAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$ ; Susilawati and Ward, 2006; Permana et al., 2013; Dai et al., 2018b), usually occur, but not necessarily exclusively, in higher-rank coals (e.g., Daniels and Altaner, 1990; Susilawati and Ward, 2006; Permana et al., 2013; Dai et al., 2017, 2018b, 2018c; Zhao et al., 2018).

In addition to anatase, rutile, and ilmenite, clay minerals (such as kaolinite and illite) may host a large proportion of Ti in some coals (Minkin et al., 1979; Ward et al., 1999; Dai et al., 2015b). Two modes of Ti occurrence were observed in the kaolinite in coal: substituting for Al in the crystal lattice of the kaolinite and as fine-grained discrete particles in kaolinite. About 1.5% Ti was suggested to substitute for Al in the kaolinite in the coal from the Gunnedah Basin, Australia (Ward et al., 1999).

Huggins et al. (2000) analyzed four coals using XAFS spectroscopy and a selective leaching protocol supplemented by SEM. They found that both methods indicate two principal forms of Cr in the bituminous coals: the major occurrence of chromium is associated with the macerals as the oxyhydroxide  $\text{CrOOH}$ , whereas a second, lesser occurrence, is associated with the clay mineral, illite, which was subsequently confirmed by ion microprobe analysis.

An interesting aspect is that the primary elements that are associated with the silicates are largely benign, that is, with several exceptions they do not cause technological, environmental, or human health problems and are not on the critical element list. Sodium may appear to be an exception as it does contribute to boiler fouling but it appears that organically-bound and non-mineral-bound Na, is primarily to blame (Finkelman, 1988). Some critical elements, such as Al and Ga, are the other exceptions as they have been industrially extracted from Al-Ga-rich fly ash derived from the coals in the Jungar deposit, Inner Mongolia, China (Seredin, 2012; Dai and Finkelman, 2018; Dai et al., 2018d). Another exception is Mg in coal, which has been recovered from fly ash derived from low-rank coals in southeastern Australia, using a combined hydrometallurgical/thermal reduction process (Dai and Finkelman, 2018).

### 3.2. Sulfides and selenides as hosts of chemical elements

A wide range of sulfide minerals have been found in coal (Table 1; Fig. 1) with pyrite being, far and away, the most common. Without question pyrite has greatest impact of any mineral in coal. Among the many problems caused by pyrite are:

- Oxidation of pyrite results in costly acid mine drainage problems (Campbell et al., 2001; Weber et al., 2006; Shahhosseini et al., 2017; Stewart et al., 2017).
- Volatilization of pyrite contributes to acid rain and smog (Dai et al., 2002; Miller, 2017).
- The iron and sulfur from pyrite are major contributors to boiler slag (Boal III et al., 1995; Brink et al., 1994; Regina et al., 2004).
- Pyrite is likely a major contributor to Coal Workers Pneumoconiosis (Black Lung Disease) (Huang et al., 2006).
- Removal of pyrite is a primary objective of coal cleaning (Duan et al., 2017; Kolker et al., 2017b; Oliveira et al., 2013).
- Proper disposal of pyrite and products of pyrite decomposition (coal cleaning wastes, boiler slag, fouling deposits, bottom ash, FGD, fly ash, etc.) adds costs to the utilization of coal.

In most coals, sulfide minerals are likely the primary host of S, Sb (55%/30%; data for disulfides leached by nitric acid and mono-sulfides leached by hydrofluoric acid), As (> 70%/55%), Cd (90%/90%), Co (55%/40%), Cu (75%/60%), Fe (50%/20%), Pb (90%/60%), Hg (90%/75%), Mo (55%/15%), Ni (55%/50%), Se (70%/20%), W (50%/20%), and Zn (75%/70%) (Finkelman et al., 2018).

Leaching coals with nitric acid (Finkelman et al., 2018), microprobe analysis (Kolker et al., 2000) and Laser ablation ICP-MS (Kolker et al., 2017a) showed that sulfides, likely pyrite, are the primary host of As and Hg, with pyrite commonly containing up to several weight percent As. Arsenopyrite has been reported in coal (Belkin et al., 1997; Kolker, 2012), but this mineral is exceedingly rare and is not a major host of As. Other elements that are likely associated with the sulfide minerals are Te, Tl, Ag, and Bi.

In addition to pyrite, important sulfide minerals include: galena, the host for Pb (55%/50%); sphalerite, the host for Cd (60%/80%) and Zn (45%/55%); and chalcocite (Fig. 1A), the host for Cu (30%/30%) (Finkelman et al., 2018). Other sulfide minerals include (Table 1): the linnaeite group ( $\text{Co}^{2+}\text{Co}_2^{3+}\text{S}_4$ ), which contains Co and Ni; marcasite ( $\text{FeS}_2$ ); pyrrhotite ( $\text{Fe}_7\text{S}_8$ ); and possibly argentite ( $\text{Ag}_2\text{S}$ ); as well as rare getchellite ( $\text{AsSbS}_3$ , Fig. 1D; Dai et al., 2006b), alabandite ( $\text{MnS}$ ; Dai et al., 2007), pentlandite ( $(\text{Fe}, \text{Ni})_9\text{S}_8$ ; Belkin et al., 2010), greenockite ( $\text{CdS}$ ; Hower et al., 2018b), selenio-galena ( $\text{PbSeS}$ , Fig. 1F; Dai et al., 2006a); pyrrhotite ( $\text{Fe}_7\text{S}_8$ ), millerite ( $\text{NiS}$ ), and siegenite ( $(\text{Ni}, \text{Co})_3\text{S}_4$ , Fig. 1B) (Dai et al., 2015f); catterite ( $\text{CoS}_2$ , Fig. 1B; Dai et al., 2015f), cinnabar ( $\text{HgS}$ ; Dvornikov, 1990), and greigite ( $\text{Fe}_3\text{S}_4$ ; Havey and Ruch, 1984).

Kolker (2012) comprehensively reviewed the distribution trace elements (such as As, Hg, Se, Sb, Mo, Tl, Cu, Zn, Co, and Ni) in iron

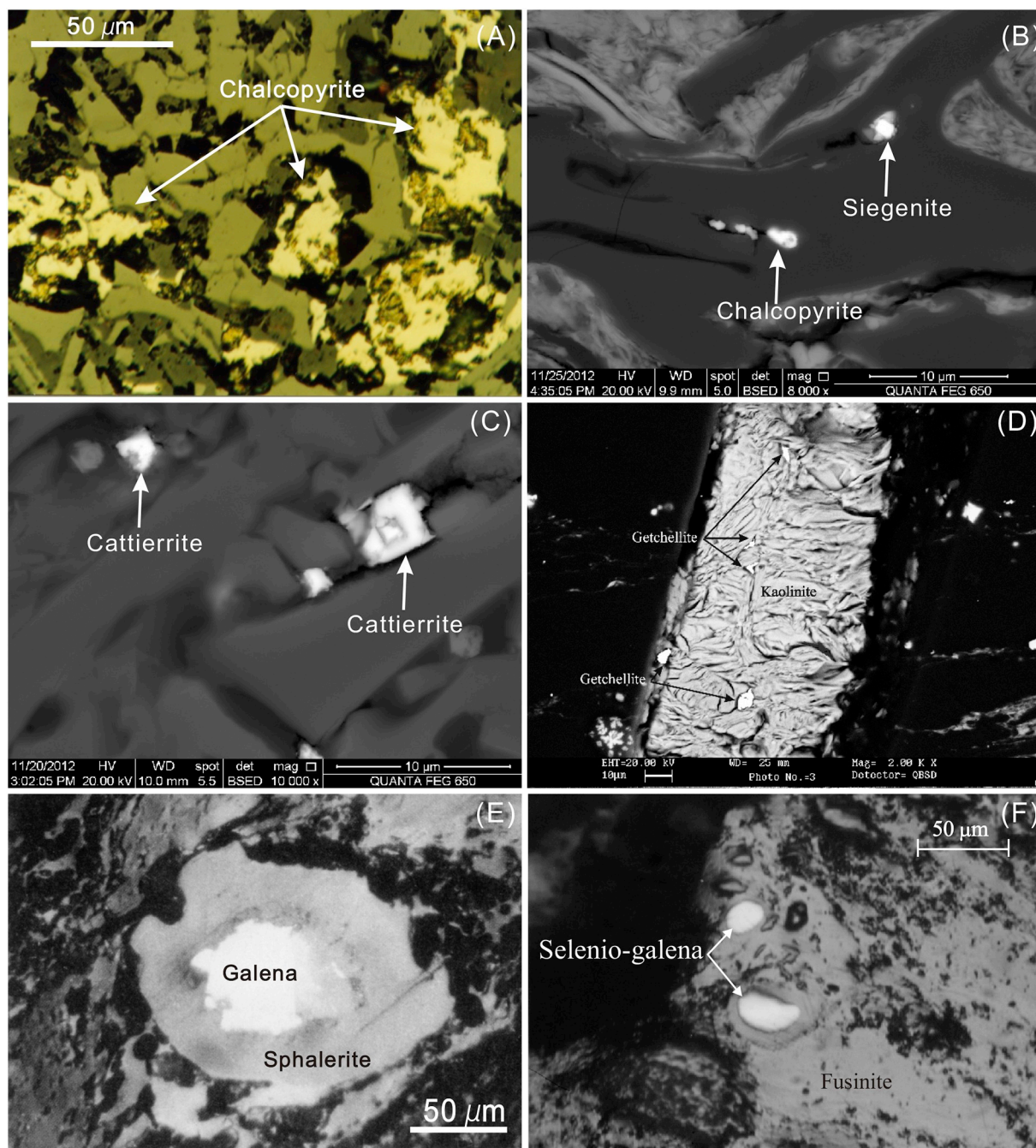


**Fig. 1.** Sulfides and selenio-galena and getchellite in coal. (A), chalcopyrite in the coal from Muchuan, Sichuan (Reflected light) (Ren et al., 2006). (B), siegenite and chalcopyrite in cavities of the Jurassic coal from the Yili deposit, Xinjiang, northwestern China (Dai et al., 2015f). (C), cell-filling cattierite in the Jurassic coal from the Yili deposit, Xinjiang, northwestern China (Dai et al., 2015f). (D), getchellite and fracture-filling kaolinite in the Late Permian coal from Xingren, southwestern Guizhou, China (Dai et al., 2006b). (E), galena and sphalerite in the Late Triassic anthracite in the Jianou Coalfield, Fujian Province in southeastern China (Ren et al., 2006). (F), selenio-galena in the Late Paleozoic coals from the Jungar Coalfield, Inner Mongolia, northern China (Dai et al., 2006a). (A), (E) and (F), reflected light. (B), (C), and (D), SEM backscattered electron images.

disulfides in coal. Analysis of coal samples in the U.S. Geological Survey's WoCQI database (Bragg et al., 1997) showed that As is the most abundant minor constituent in Fe-disulfides in coal and elements including Se, Ni, and other minor constituents are less-commonly present with lower concentrations than As. Fe-disulfides with different generations (different formation stages) or different origins may have different abundance of trace elements (Kolker, 2012). For example, framboidal pyrite in some instances shows preferential Ni enrichment with respect to other co-occurring pyrite with other modes of occurrence (e.g., cleat- or vein-filling pyrite or marcasite; Kolker, 2012).

Using high-resolution time-of-flight secondary ion mass-spectrometry, Dai et al. (2003) investigated the abundance of trace elements in different-form pyrites, such as bacteriogenic, framboidal, massive, cell-filling, fracture-filling, and nodular pyrites. They found that relative to other form pyrite, bacteriogenic pyrites are rich in Cu, Zn, and Ni, and this is consistent with bacterial complexing of metals in anoxic sediments (Kolker, 2012).

When trace elements such as As, Se, and Sb are present in pyrite, they usually substitute for S of pyrite, whereas transition metals, such as Hg and Pb, are thought to substitute for Fe of pyrite (Kolker, 2012).

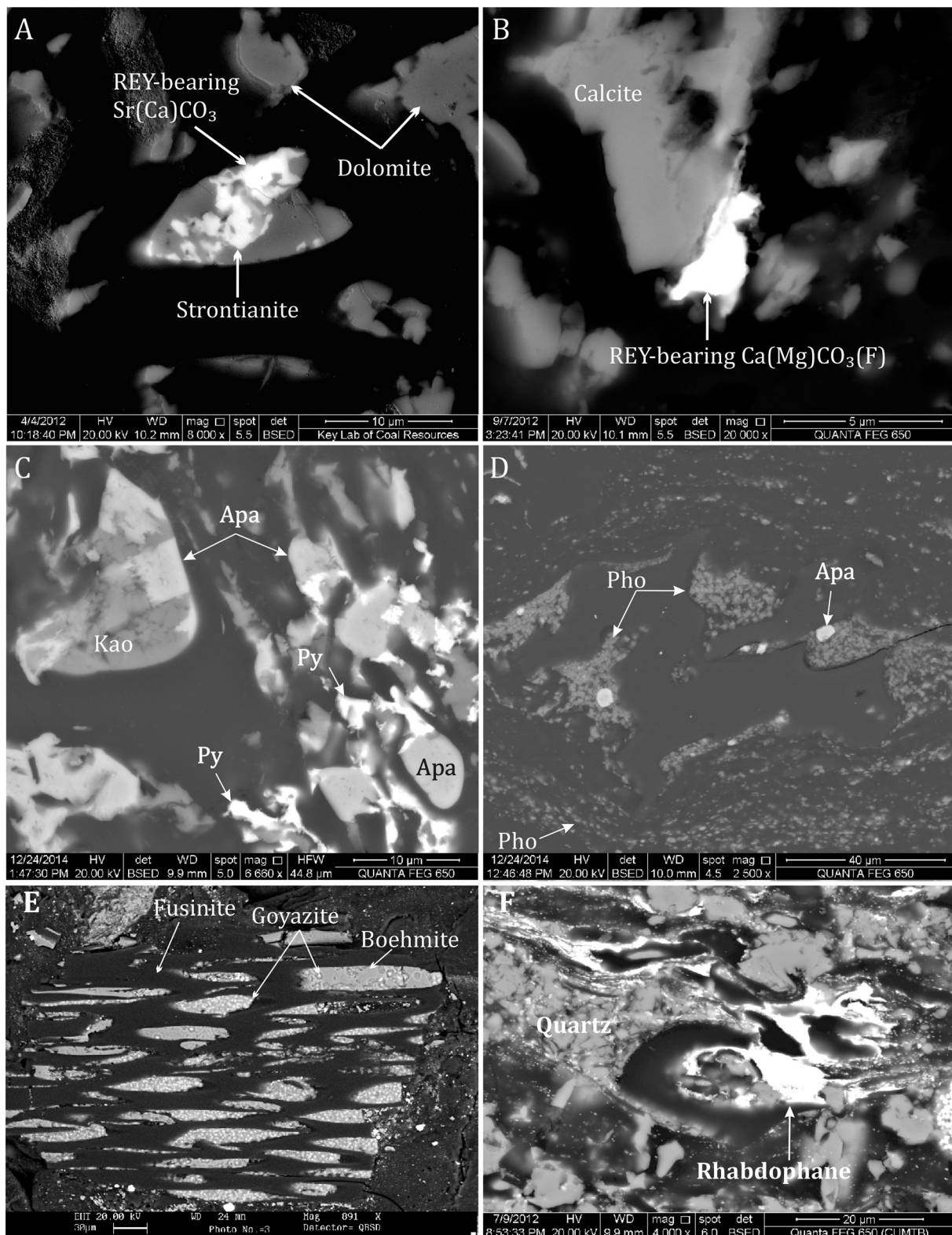


**Fig. 2.** Carbonate and phosphate minerals in coal. (A), REY-bearing carbonate mineral ( $\text{Sr}(\text{Ca})\text{CO}_3$ ), strontianite, and dolomite filling the fusinite cells in the Late Permian coal from the Heshan Coalfield, southern China (Dai et al., 2013a). (B), REY-bearing carbonate mineral ( $\text{Ca}(\text{Mg})\text{CO}_3(\text{F})$ ) in the Late Permian coal from the Heshan Coalfield, southern China (Dai et al., 2013a). (C), Apatite (Apa), kaolinite (Kao), and pyrite (Py) filling the fusinite cells in the middle Jurassic coal from the Muli Coalfield on the Tibetan Plateau, China (Dai et al., 2015a). (D), Apatite and aluminophosphrous minerals of goyazite-gorceixite-crandallite group (Pho) filling fusinite cells in the Muli Coalfield on the Tibetan Plateau, China (Dai et al., 2015a). (E), Goyazite and boehmite filling the fusinite cells in the Late Paleozoic coals from the Jungar Coalfield, Inner Mongolia, northern China (Dai et al., 2006a). (F), rhabdophane in collodetrinite in the late Permian coal from the Huanyingshan Coalfield, Sichuan, southern China (Dai et al., 2014b). SEM backscattered electron images.

However, a recent study by Etschmann et al. (2017) showed that As has a more complex speciation pattern than expected. Arsenic may have several valence states such as As(III), As(V), and As(−I/+II) in solid solution in sulfides in coal. Arsenic may occur in anionic and cationic forms, i.e., it shows both the common substitution for S and the substitution for Fe.

Some selenides have been identified in coal. Relative to other selenides, clausthalite (PbSe) a very common accessory mineral in coal is a host for Pb and Se (Finkelman, 1985; Hower et al., 2001; Yudovich and Ketris, 2006a; Belkin et al., 2010; Dai et al., 2006a, 2015f; Karayığit et al., 2018). Hower and Robertson (2003) and Dai et al. (2006a) showed that clausthalite, if present in coal, contributes not only to the elevated concentrations of Pb and Se content, but also to Hg concentration in the coal. Other selenides reported in coal include: ferroselite (FeSe<sub>2</sub>; Dai et al., 2015f), krutaite (CuSe<sub>2</sub>; Dai et al., 2015f), eskebornite (CuFeSe<sub>2</sub>; Dai et al., 2015f), and tiemannite (HgSe; Dvornikov, 1990; Finkelman, 2003).

### 3.3. Carbonates as hosts of chemical elements

Carbonates are present in many, but not all, coals (Fig. 2). The most common carbonate minerals are calcite (CaCO<sub>3</sub>), siderite (FeCO<sub>3</sub>), and ankerite-dolomite series (Ward, 2016). When present, the carbonates could be major hosts for Ca, Mg, Fe, Mn, and Sr, and to a lesser extent, rare earth elements (REE) and F (Swaine, 1990; Finkelman et al., 2018), and in a few cases, Zn (e.g., calcite, Palmer and Wandless, 1985). Leaching coals with hydrochloric acid indicates the following associations: Ba (15%/75%), Ca (70%/60%), Fe (25%/ < 60%), Mg (25%/30%), Mn (50–85%/75%), Mo (15%/ < 20%), REE (10– < 30%), and Sr (< 50%/ < 50%) (Finkelman et al., 2018).

Mn<sup>2+</sup> substituting for Fe<sup>2+</sup> (siderite, ankerite) and Ca<sup>2+</sup> (calcite and ankerite) and Sr<sup>2+</sup> substituting for Ca<sup>2+</sup> (calcite) have been observed in many coals (e.g., Swaine, 1990). Other carbonates observed in coals include aragonite (CaCO<sub>3</sub>), witherite (BaCO<sub>3</sub>), strontianite (SrCO<sub>3</sub>; Fig. 2A), dawsonite (NaAlCO<sub>3</sub>(OH)<sub>2</sub>), and members of the bastnäsite ((Ce,Lu)CO<sub>3</sub>F, (La, Ce)CO<sub>3</sub>F, or (Y, Ce)CO<sub>3</sub>F) series. Dai et al. (2017) have identified one of REE hosts, bastnäsite, in the late Permian coals from the Moxinpo Coalfield, southwestern China. Dai et al. (2013a) identified REE-bearing carbonates, Sr(Ca)CO<sub>3</sub> and Ca(Mg)CO<sub>3</sub>(F) (Fig. 2B) containing U in the late Permian coals in the Heshan Coalfield, southern China. In addition to F in many cases occurring in REE-bearing carbonate (such as bastnäsite), Cl can also occur in carbonate (Yudovich and Ketris, 2006b).

### 3.4. Oxides and (oxy-)hydroxides as hosts of chemical elements

The most common oxide minerals in coal are rutile and its polymorphs anatase and brookite (e.g., Cressey and Cressey, 1988), which are important hosts of Ti (35%/15%; Finkelman et al., 2018). Detrital ilmenite (Fe<sup>2+</sup>TiO<sub>3</sub>) and chromite (Fe<sup>2+</sup>Cr<sub>2</sub><sup>3+</sup>O<sub>4</sub>) are in some cases present and could be important hosts of Ti and Cr (e.g., Mullai, 1984; Ruppert et al., 1996). It is likely that Ta (75%/60%) is hosted by oxides, as well as the geochemically similar Nb, but few of these minerals have been reported in coal. Several molybdenum oxides have also been reported (Gluskoter, 1977; Cobb et al., 1979). Other oxide and (oxy-)hydroxides minerals reported from coal include: Fe hosts such as magnetite (Fe<sub>3</sub>O<sub>4</sub>; e.g., Pollock et al., 2000), limonite (FeOOH·nH<sub>2</sub>O; e.g., Swaine, 1990), hematite (Fe<sub>2</sub>O<sub>3</sub>; e.g., Silva et al., 2011), lepidocrocite (Huggins et al., 1980); and Al hosts such as boehmite (Ward, 2002; Dai et al., 2006a), diaspore (Dai et al., 2012a), and goethite (Huggins et al., 1980). Corundum (Al<sub>2</sub>O<sub>3</sub>) is usually rare in coal (Finkelman, 1988; Vassilev et al., 1994) but in some cases it is an accessory minerals in fly ashes (Dai et al., 2010; Vassilev et al., 2003, 2005) and high-temperature ashes (Ward, 2002), particularly in those derived from coals with elevated concentration of Al (e.g., Dai et al., 2010; Hu et al., 2018; Ward, 2002, 2016). Corundum is a characteristic

mineral in high-alumina fly ash derived from alumina-rich feed coals (e.g., boehmite-bearing coals; Dai et al., 2010). The Nb and Sn hosts, columbite ((Fe,Mn)Nb<sub>2</sub>O<sub>6</sub>) and cassiterite (SnO<sub>2</sub>), respectively, have also been reported (Merritt, 1988).

The fly ash derived from a Chinese Al-Ga-REY coal-hosted ore deposit (Jungar Coalfield, Dai et al., 2006a, 2012c) has been utilized for Al and Ga extraction because it contains > 50% Al<sub>2</sub>O<sub>3</sub> and ~100 ppm Ga. One of the major hosts for Al and Ga is oxyhydroxide (e.g., boehmite and diaspore; Dai et al., 2006a, 2012c).

### 3.5. Phosphates as hosts of chemical elements

Phosphate minerals in coal are ubiquitous. The most common is apatite (or fluorapatite; Fig. 2C, D) but monazite, xenotime, and the alumino-phosphate mineral group (crandallite, florencite, gorceixite, and goyazite; Fig. 2E) are also present in most coals (Dai et al., 2015a, 2018a; Ward, 2016). They are important hosts of P (95%/85%), Ba (< 45%/ < 15%, Sr (50%/50%), and U (15%/5%) (Finkelman et al., 2018). Apatite in coal is usually fluorapatite, indicating that some OH<sup>−</sup> in the former has been replaced by F<sup>−</sup>.

In addition to Ca, Ba, Sr, P, Al, and U, the phosphates are also an important host of REE and Y (e.g., xenotime, Dai et al., 2017; Seredin and Dai, 2012; Y-, La-, Ce-, Nd-, Dy- and Gd-bearing apatite and Y-bearing crandallite, Hower et al., 2016; light rare earth elements, 70%/20%; heavy rare earth elements, 50%/25%, Finkelman et al., 2018), and F in the phosphate minerals (apatite, Dai et al., 2015a). Although not common, rhabdophane (Fig. 2F) and silico-rhabdophane, the major light rare earth element hosts, have been identified in many coals (Dai et al., 2014b). Chlorine and Br may be present in gas-liquid inclusions of detrital and authigenic apatite (Vassilev et al., 2000); however, as pointed out by Yudovich and Ketris (2006b), Cl with such modes of occurrence seems to be very minor.

### 3.6. Halides and fluorides as hosts of chemical elements

Several halide minerals have been observed in coal, the most common being halite (NaCl) and sylvite (KCl) and host Na, K and Cl (e.g., Cressey and Cressey, 1988; Vassilev et al., 1994; Mudd and Kodikara, 2000; Yossifova et al., 2011; Fu et al., 2013; Oskay et al., 2016). The occurrence of halite has been confirmed using XRD by some authors (e.g., Kalaitzidis et al., 2010; Karayığit et al., 2015). The fluoride that has been found in coal is fluorite (CaF<sub>2</sub>), which has seldom been observed in coal (Yudovich et al., 1985; Finkelman, 1995; Bouška and Pešek, 1999; Dai et al., 2013a, 2018c), but is the major cause of elevated concentration of F in coal (Dai et al., 2013a, 2018c).

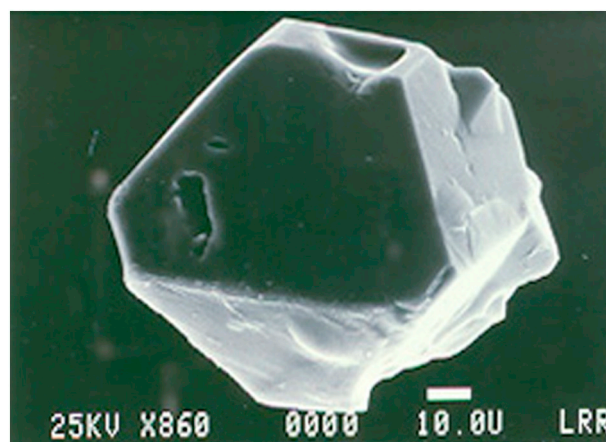


Fig. 3. Detrital diamond extracted from a bituminous coal from Powder River Basin (SEM image).

### 3.7. Sulfates as hosts of chemical elements

Sulfates are not uncommon in coal and most are secondary oxidation products. The most common syngenetic sulfates in coal are gypsum (Ward, 2002, 2016; Liu et al., 2018) and barite (Finkelman et al., 2018).

Sulfates are the hosts of some major elements in coals (Table 1), for example, Ca (gypsum, basanite, anhydrite), Fe (coquimbite, melanterite, rozenite, szomolnokite), K (jarosite), Al (alunite, alunogen, aluminite, tschermigite), Na (thenardite, glauberite, bloedite), Mg (epsomite, hexahydrate, copiapite, pickeringite). Additionally, sulfates are hosts for a few trace elements, e.g., Sr (celestite) and Ba (barite, (> 25% / < 15%; Finkelman et al., 2018). Dai et al. (2015e) have identified a hydrous Be sulfate phase ( $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ ) in coal LTA samples with elevated Be concentrations in the Lincang deposit, southwestern China, and the content of the Be sulfate phase is up to 6.2% (LTA basis). It should be noted that gypsum in coal usually contains some Sr, and if the Sr-contained gypsum is of syngenetic origin, the isotopic compositions of Sr could be used as an indicator for geochronology and palaeoenvironment of peat deposition (Spiro et al., 2019).

### 3.8. Interesting but rare associations

Seredin and Finkelman (2008) reported many unusual mineral phases, including native W, Au and Ag,  $(\text{BiPb})_3\text{FeCdMoS}$ ,  $\text{BiMo}(\text{Cu})\text{S}$ , various Au and Pt phases, primarily in Russian coals. Hower et al. (2018b) found in the Blue Gem coal in Kentucky grains containing Co–Ge and Ag–Cd–Bi, the latter with a more evident S association than the former, metallic Bi,  $\text{Ni}_3\text{Sn}$ , and silver cadmium. These strange and interesting phases may have economic and geochemical significance, but are not likely to represent significant common modes of occurrence of these elements in coal. Other interesting but rare mineral occurrences include:

- Amphibole containing F or/and Cl -  $\text{NaCa}_2(\text{Mg,Fe,Al})_5(\text{Si,Al})_8\text{O}_{22}(\text{OH,F,Cl,O})_2$  (Finkelman, 1981; Brownfield et al., 1995; Kortenski and Sotirov, 2004; Papanicolaou et al., 2004; Yossifova, 2007).
- The Ca-bearing oxalates weddellite ( $\text{Ca}(\text{C}_2\text{O}_4) \cdot (2.5-x)\text{H}_2\text{O}$ ,  $0 \leq x \leq 0.25$ ) and whewellite ( $\text{Ca}(\text{C}_2\text{O}_4) \cdot \text{H}_2\text{O}$ ) (Bouška, 1981; Bouška et al., 2000; Zák and Skála, 1993; Goodarzi, 1990; Koukouzas et al., 2010; Dai et al., 2015c).
- Diamond – carbon (Fig. 3)
- Rare native sulfur in coal (e.g., Erkoyun et al., 2017; Ribeiro et al. (2016) but common in spontaneous combustion products (e.g., Fabiańska et al., 2013; Gürdal et al., 2015).

### 3.9. Uncertain associations and issues that need further attention

Although modes of mineral occurrence of a number of elements have been widely investigated, there are some elements whose associations and particularly association mechanism with minerals are, to a degree, uncertain or even largely unknown and deserve further attention. These include but not limited to Be, Bi, B, Br, Cs, Co, Au, I, In, Mo, Ni, Nb, the platinum group elements, Ag, Ta, Te, Tl, Th, Sb, W, and V.

## 4. Conclusions

Minerals are the most important components of inorganic matter in coal and, in most cases, play the most significant role in affecting the utilization of coal. Minerals are also the major hosts of the vast majority of toxic, benign, and critical elements present in coal. Although a number of elements and their hosting minerals in coal have been widely investigated, some issues require further investigation to evaluate more fully the modes of occurrence of elements in coal:

- The associations of some elements with minerals are uncertain or even largely unknown (for examples but not limited to Be, Bi, Br, Co, I, In, Mo, Nb, Ta, Te, W, and V) and deserve further investigation using integrated approaches as mentioned in the text above.
- The association mechanism of many elements with minerals are also unknown, e.g., conditions of toxic elements (As, Hg, Tl) substitute for major ions of sulfides in coal.
- Quantitative analysis of elements associated with specific minerals rather than with generic terms such as ‘clays’, ‘silicates’, and ‘carbonates’ needs new technologies for more fully understanding modes of occurrence of elements.
- As mentioned in Section 3.8 a number of interesting and rare phases have been found in coal confirming that additional detailed mineralogical investigations of coal are entirely justified.

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