cies (particularly the Saltwater crocodile) are highly pugnacious and regularly fight with their own species.

Suggestions for further reading

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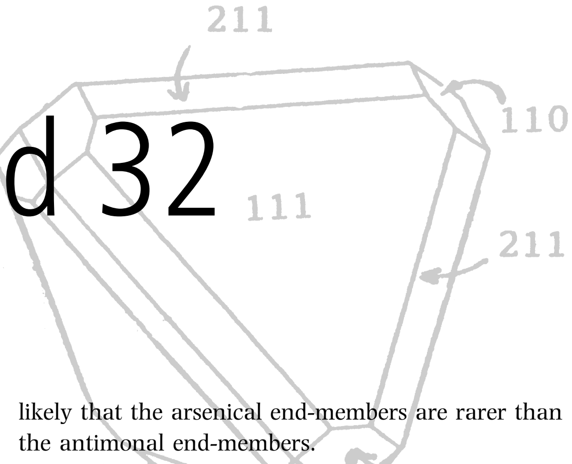


The tetrahedrite group

R. J. King

The tetrahedrite group is a member of a family not yet examined in *Geology Today*, the sulphosalts. The term ‘sulphosalt’ is used to indicate a certain type of unoxidized sulphur mineral that is structurally distinct from a sulphide. The family is diverse and quite large, with over a hundred species. Its members differ from sulphides, sulpharsenides and arsenides, as the semi-metals As, Sb and Bi in the formula act rather like metals in the structure. They may be thought of as double sulphides.

The members of the tetrahedrite group form a prominent group of non-stoichiometric compounds within the sulphosalt family, with variable ratios of metals, semi-metals and sulphur. In the group there are essentially seven sites or end-members with, however, at least 48 other possible sites and with the exotic possibility far beyond that number. For example, there are said to be 27 end-members of the group in the complex ore of the Sark Hope mine in the English Channel Islands. As a result there are many synonyms. Space here demands that we should be realistic, but also that we should look at the nomenclature in conjunction with the formulae.

The group is often described under the title ‘the Fahlores’, a useful field name taken from the part spelling of the old German word *fahlerz* for grey-coloured and ore. This is a useful term if only for the fact that members of the group are almost impossible to differentiate visually, being so similar crystallographically and physically. From observation it is likely that the arsenical end-members are rarer than the antimonal end-members.

The fahlores are geographically universal and occur in many geological environments, but relatively few occur in well-developed crystals.

The chemistry of the fahlores

The group is notable for the wide variety of elements which are stable in its structure. The formula may be written as A_{12},B_4,X_{13}, where A = Ag,Cu,Fe,Hg,Zn; B = As,Sb,Te; X = S,Se,Te. The Sb–As elemental components form a complete series from tetrahedrite to tennantite, with ratios being essentially Sb : As = 1 : 1. Species designators are at present based on the elements which constitute the pluarity of occupation in the combined sites of A, B and X. Thus species formulae may be erected:

tetrahedrite, $(Cu,Fe,Ag,Zn)_{12}Sb_4S_{13}$;
tennantite, $(Cu,Ag,Fe,Zn)_{12}As_4S_{13}$;
argentotennantite, $(Ag,Cu)_{10}(Zn,Fe)_2(As,Sb)_4S_{13}$;
freibergite, $(Ag,Cu,Fe)_{12}(Sb,As)_4S_{13}$;
giraudite, $(Cu,Zn,Ag)_{12}(As,Sb)_4(Se,S)_{13}$;
goldfieldite, $Cu_{12}(Te,Sb,As)_4S_{13}$;
hakite, $(Cu,Hg)_{12}Sb_4(Se,S)_{13}$.

Tetrahedrite, $(Cu,Fe,Ag,Zn)_{12}Sb_4S_{13}$, was so named by Haidinger in 1845 in allusion to its tetrahedral morphology. The synonyms panabase, clinoedrite, fahlite, nepaulite, struderite, falkenhaynite and stylotypite are discredited. The last named has been shown to be a mixture. It was named from the Greek for pillar to account for its columnar habit. Other synonyms include coppite, used previously to denote the presence of < 13% Fe. The name was given in honour of P. Coppi, the owner of a Tuscan mine. The name frigidite was given to a supposed variety of tetrahedrite containing Ni from the Frigido Valley in Italy. A commonly used name, schwatzite, is a variety of tetrahedrite containing up to 17% of Hg, so named from its original locality, Schwaz, in the Austrian Tyrol. The name malinowskite is a mixture, which accounts for the anomalous presence of Pb. Au is frequently present as the native metal in massive ore or in fractures transported by the thiosulphate ligand. It is rarely present in tennantite.

Tennantite, $(Cu,Ag,Fe,Zn)_2As_4S_{13}$, was so named in 1819 to honour the English chemist Smithson Tennant. The synonyms arsenicalfahlerz, julianite and fredricite have been discredited. The variety annivite, named after the Anniver Valley in Switzerland, is a variety of tennantite containing < 13% Bi. It is often used in Russian literature in the role of an end-member. A possible retrogressive step takes the form of re-naming the Zn-bearing variety of tennantite, Sanbergite (Breithaupt), to the locality name Miedziankite, although both are discredited. In conversing with Swiss dealers and collectors it is important to use the synonym of tennantite, binnite (of Des Cloizeaux), from the locality Binntal in Switzerland.

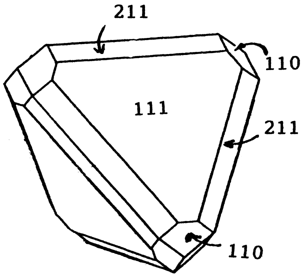
Argentotennantite, $(Ag,Cu)_{10}(Zn,Fe)_2(As,Sb)_4S_{13}$, is an end-member named in 1986. Its occurrence was noted in northern Kazakhstan.

Freibergite, $(Ag,Cu,Fe)_{12}(Sb,As)_4S_{13}$, Ag-bearing end-member of the group carrying up to 18% of Ag. The name was given by Kenngott in 1853 from its locality at Freiberg in Saxony. There are discredited synonyms, including aphtonite (of Svanberg, 1848), from the Greek for abundant, referring to the Ag content; polytelite (Kobell), from the Greek for very valuable; and leukargyrite (Weisbach, 1875), from the Greek, white and silver.

Giraudite, $(Cu,Zn,Ag)_{12}(As,Sb)_4(Se,S)_{13}$, was named to honour R. Giraud in 1982. It was first described from the Puy de Dôme area of France.

Goldfieldite, $(Cu)_{12}(Te,Sb,As)_4S_{13}$, is a Te-bearing tetrahedrite, named by Ransome in 1909 after the locality in Nevada. There is doubt about the validity of this member of the group. Work in the first half of the 20th century indicated a lack of homogeneity and suggested that the material from the Claremont mine at Goldfield was a mixture.

Fig. 1. A typical tetrahedrite – tennantite crystal, showing the principal forms: the positive tetrahedron {111}, positive tristetrahedron {211}, dodecahedron {110}.



Hakite, $(Cu,Hg)_{12}Sb_4(Se,S)_{13}$, was so named in 1971 to honour J. Hak of Kutná Hora in Bohemia, from the occurrence of the mineral in a calcite vein in Předbořice in Bohemia.

Throughout the group, in addition to the complexity of elemental variation, there is the addition of trace elements such as Cd, Ga and Au.

The structure of the fahlores

All members are isostructural and of cubic symmetry, the principal morphology being the tetrahedron (Fig. 1). The latter are sometimes in groups of parallel crystals. Crystal size varies from microscopical to up to 130 mm across a face – e.g. tennantite at Tsumeb, Namibia. Members may be coarse-to-fine granular, massive and occasionally nodular.

Fig. 2. A typical crystal of tetrahedrite, showing interpenetration twinning and a partially removed coating of chalcopyrite. Silbersegen Mine, Clauthal, Germany. The crystals are 15 mm across. (Photo: Rainer Bode.)

While X-ray study determines that argentotennantite conforms structurally, it occurs in small grains up to 0.1 mm in a polymetallic deposit in Northern Kazakhstan. Giraudite occurs in microscopical grains in the Chaméano deposit in Puy de Dôme, France. Similarly, hakite occurs as xenomorphic grains up to 0.3 mm.

Twinning is common on [111] or as interpenetration twins (Fig. 2), which may be repeated as at the Kōsuke Province in Japan, where the tetrahedron face is common to two individuals to outline a six-rayed star. Other physical features of the group present in macroscopical material include the fact that there is no cleavage but a subconchoidal fracture present in massive material. Crystals tend to be brittle.

The colour of members varies from steel-grey to iron-black, often an indicator of Hg. The streak varies from black to red, a possible indicator of low Fe and high As. The lustre of crystals is sometimes splendent, but may be satiny or rough. The hardness varies from 3 to 4.5, with tennantite being slightly harder than tetrahedrite. The specific gravity varies from 4.6 to 5.1, often an indicator of an increase of Sb.

Epitaxial overgrowths of sulphides have been observed on members of the group. These include pyrite and chalcopyrite. The latter often forms satin-like sheens on crystals (Fig. 2). Classical material from the Herodsfoot Mine, near Liskeard in Cornwall, is beloved of external examiners, but controversy exists about the possibility of exsolution of the chalcopyrite. Epitaxial overgrowths of tetrahedrite often coat crystals of sphalerite and chalcopyrite. Large crystals of miargyrite ($AgSbS_2$) have been discovered encrusted with minute exsolved crystals of tetrahedrite.

Alteration of the fahlores

Tetrahedrite has been reported pseudomorphic after chalcopyrite and sphalerite after tetrahedrite. Large crystals of tetrahedrite on massive dolomite at Schwaz in the Austrial Tyrol are frequently corroded and encrusted by minute crystals of chalcostibnite ($CuSbS_2$) and antimony oxides. Hg-bearing tetrahedrite has been seen corroded to earthy malachite, azurite and cinnabar. Fine pseudomorphic crystals of enargite after tetrahedrite have been reported from Quiruvilca in Peru. The complex breakdown of tetrahedrite has been studied in detail at Broken Hill, New South Wales. As tennantite is arsenical, breakdown has produced exotic species such as olivenite and adamite, as at Carinthia in Austria and Tsumeb in Namibia. Tennantite has been reported from the English Lake District, sometimes replacing sphalerite, and subsequently replaced by covelline and hydrated copper carbonates. Fine crystals of azurite, malachite and pharmacosiderite, pseudomorphic after chalcocite and tennantite, have been mined at Tsumeb.

Distinguishing features of the fahlores

While it is almost impossible to differentiate between individual members of the group, a practised eye may venture to do so. In certain cases the complete absence of either As or Sb from an ore body may allow an observer to make a shrewd guess.

Again, a practised eye may be able to differentiate between members of the group and their associates. Galena has a silvery lustre and a marked cubic cleavage. Massive intergrowths of tetrahedrite and bournonite and/or enargite may be difficult to tell apart. Streak may help, and bournonite has two imperfect cleavages and enargite a perfect one, while members of the group have none.

Environment of the fahlores

Members of the group are probably the most widespread and economically important of the sulphosalts. Copper and argentian members add greatly to the values of an orebody. Members of the group are most commonly found in low- to medium-temperature hydrothermal bodies which are usually late in the paragenetic sequence. There are said to be exceptions to the rule, notably at Broken Hill, New South Wales, where tetrahedrite was an important primary Ag-rich mineral in the regionally highly metamorphosed ore bodies. It was also said to occur in high-temperature veins in Cornwall. It has certainly been found there in epithermal veins. There may be some aspect of telescoping in the lodes.

Contact metamorphic bodies are also said to produce higher temperature fahlores, as at Fahlun in Sweden. Members of the group occur in skarns, as at Tunaberg in Sweden and with Ag-rich galenas in the skarns of Corsica, and in the Rio Ribeira de Iguapé in southern Brazil.

Tetrahedrite has been reported from carbonatites, and tennantite from miarolitic cavities in monzonite pegmatites. In the regionally metamorphic environment, members have been found in the Grenville Province at Balmat, St Lawrence County, New York. Members of the group occur in veins in low-temperature schists, as in the Val di Susa in Italy, and low-grade schists in the Čemernica district of Bosnia.

Fahlores have been reported as occurring in Alpine fissure veins cutting quartz–muscovite schists, as at Usseglio, Piedmont, in Italy. Tetrahedrite has been seen in association with zeolites at Stainchol on the Isle of Skye. Members of the group are important members of sedimentary exhalative deposits – e.g. in the Neogene–Quaternary volcanic complex of the central Andes, north-east Turkey, and at Långdal in northern Sweden.

Tetrahedrite occurs in sediments as nodules and veins with chalcocite and chalcopyrite at Sandlodge Mine on the Mainland of the Shetland Isles. It has also been observed in dolomites in the Muschelkalk at

Weisloch in Heidelberg, associated with tennantite. It has been suggested that biogenic processes are at work here. Metasomatic processes have been invoked to account for the occurrence of tetrahedrite as disseminations in dolostone and limestone at Kalkar, Santa Cruz in California and at Mirgalinsay in southern Kazakhstan in Russia.

Fahlores are forming today. They have been identified in the scale forming on the walls of hydrothermal wells in southern Hokkaido in Japan at a temperature of 260 °C. They have also been identified on the Juande Fuca Ridge as the product of interaction between hydrothermal fluids and sea water.

Perhaps the most remarkable deposit of tennantite was in the Tsumeb mines of Namibia. There, large tetrahedral crystals up to 130 mm across and large steel-grey masses with a high lustre occurred in both primary and secondary deposits in the mines. The complex single crystals of binnite (tennantite) of Switzerland in meta-dolomite were the result of deposition from slowly cooling aqueous solutions during the Alpine orogeny.

Where to find fahlores

The recently described members of the group are at present single-locality material. In the past, Britain has produced classical material, but there is little hope that it will do so again in the future. It is as well, therefore, to watch dealers' catalogues, which could be rewarding if the necessary capital is available. High on the list must be Cornish material, especially that from Herodsfoot mine near Liskeard.

It is just possible that poorly crystallized material will be found in old mining areas, such as Tomnadashan in the Tayside district of Scotland, and at the Paddy End section of the mine at Coniston in Cumbria. There are several references to members of the group in the English Lake District, including the Caldbeck Fells, though not as well-developed crystals. There are two references to tetrahedrite occurring in Derbyshire; one is stated to be crystallized. It was common in Gortdrum mine in the Silvermines area of Tipperary in Ireland and massive material is readily available from dealers.

Up to the 1960s, pyrite often accompanied by well-crystallized tetrahedrite, was readily available from numerous mines in the Peruvian and Bolivian mining fields, especially from Quiruvilca and Huaron in the Cerro de Pasco of Peru and Huanchaca in Bolivia. While the bulk of material has now been dispersed, much remains and is frequently available for sale at mineral shows.

While material from the tetrahedrite group is often produced at mine sites and quarries, it is usually necessary to be at the right place at the right time. For example, a large tennantite–galena vein with a well-developed array of arsenical oxidation products was surprisingly exposed recently in a quarry in the Welsh Borderlands.

Uses of the fahlores

By far the greatest use is as ores of copper and silver. Ag-rich members present in an ore deposit greatly enhance its richness, especially if oxidation has taken place. It has also been suggested that members of the group could have potential in the fields of geothermometry and geobarometry.

Many members of the group carry varying proportions of mercury. Geochemical prospecting in the Mitterberg ore deposit near Salzburg in Austria has shown that its presence produces a significant Hg anomaly in the overlying sedimentary cover, even at thicknesses of 500 m.

Faking in the fahlores

Old specimens from Swiss dealers and strahlers are often found to be faked. It was not then considered to be unethical to falsify mineralogical material. Pink fluorite was often skilfully glued onto Alpine Fissure veins and binnite (tennantite) onto suitable dolomite substrates. Nowadays, with the creation of the Bôrsenaufsicht (Bourse police), it is not so easy for dealers or private collectors to pass Swiss fakes off as being genuine.

Curation of the fahlores

Sulphides are often intimately associated with members of the group and their behaviour should be carefully monitored. Such associations are often prone to disruptive attack, especially if the curatorial atmosphere is unsuitable. Some members of the group are liable to attack through the action of light. The splendent iron-black crystals of tetrahedrite – tennantite from Morococha, Peru, soon become dull on exposure to light.

As with many sulphides, members of the group quickly lose lustre if subjected to attack by tobacco smoke, especially that of cigarettes. Such attack can be rapid and cannot be reversed.

Suggestions for further reading

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As you were: 'Geothermal energy comes from many sources. Initially, the Earth was one big ball of molten rock, formed by the gradual accretion of rock and dust. Some geothermal heat is from cooling after that formation stage.' – *The Independent*, 18 February 1997.