

Crystal chemistry of the crandallite, beudantite and alunite groups: a review and evaluation of the suitability as storage materials for toxic metals

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The crandallite, beudantite and alunite (jarosite) mineral groups are reviewed, with an emphasis on the evaluation of their suitability as storage materials for toxic metals. New data on the highly flexible crystal chemistry, crystallography and thermodynamic stability fields of both natural and synthetic members are summarised and critically discussed. These compounds can safely incorporate a large number of toxic and radioactive metals. Extensive solid solubilities have been observed. The majority of the members are characterised by very low solubilities over a wide range of pH and Eh conditions, and by high temperature stabilities (up to 400–500°C). It is suggested, also by comparison with other mineral waste hosts (apatites, pyrochlores), that these materials can be favourably used for the long-term fixation and immobilisation of toxic ions of elements such as As, Pb, Bi, Hg, Tl, Sb, Cr, Se, and of radioactive isotopes of K, Sr, Th, U and REE.

Introduction

The crandallite $[\text{CaAl}_3(\text{PO}_4)_2(\text{OH},\text{H}_2\text{O})_6]$, beudantite $[\text{PbFe}_3(\text{AsO}_4)(\text{SO}_4)(\text{OH},\text{H}_2\text{O})_6]$ and alunite (jarosite) $[\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6 (\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6)]$ groups belong to the alunite supergroup, a large family of minerals and synthetic analogues, all of which share the basic, rhombohedral structure type of alunite, $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$ (Wang et al., 1965; Menchetti and Sabelli, 1976). The pronounced crystal-chemical versatility of this supergroup is expressed by the general formula $AB_3(XO_4)_2(\text{OH},\text{H}_2\text{O})_6$, where A =mono-, di-, tri- or tetravalent cation, B =trivalent cation, and minor amounts of certain di- and pentavalent cations, and X =penta-, hexavalent cations and minor Si^{4+} .

In view of recent data on alunite-type compounds, their use as storage materials (minerals) for toxic and

radioactive metals is suggested and their suitability as stable host structures for these metals will be discussed in the present review. The underlying concept of this “synthetic mineral immobilisation technology” (SMITE) is very old (Hatch, 1953) and currently a variety of mineral structure types are employed or have been proposed for the incorporation of various waste materials (the following list is not intended to be exhaustive):

For the immobilisation of high level nuclear wastes, the well-known Synroc ceramic matrix, consisting of the titanates zirconolite, $\text{CaZrTi}_2\text{O}_7$, hollandite, $\text{Ba}(\text{Al},\text{Ti})_2\text{Ti}_6\text{O}_{16}$, and perovskite, CaTiO_3 , has been proposed and successfully tested (e.g., Ringwood et al., 1979; Jostons and Kesson, 1994). It is able to safely incorporate radioactive elements from the lanthanide and actinide series, as well as Cs, K, Sr and others, but is yet to be adopted by the nuclear industry for the permanent disposal of waste. Apatite-type compounds are used to remove heavy metal contaminants from wastewater, aquatic solutions and soils, to stabilise toxic metals in

waste dumps and to immobilise radioactive waste (e.g., Suzuki et al., 1985; Gauglitz et al., 1992; Ma et al., 1993; Xu and Schwartz, 1994; Carpena and Lacout, 1997; Traina and Laperche, 1999). A synthetic ceramic matrix designated Xtaltite has been devised to deal with Pb-, As- and Sb-rich ore smelter wastes in Australia; in a hydrometallurgical treatment Ca is added to the primary waste materials and a calcining process produces a ceramic composed of apatite-type $(\text{Pb,Ca})_5(\text{AsO}_4)_3(\text{OH,Cl})$ (corresponding to calcian hydroxyl-mimetite) and pyrochlore-type $\text{Ca}_2\text{Sb}_2\text{O}_7$ (corresponding to romeite) (e.g., White and Kyle, 1995; White et al., 1995). Selected zeolites are employed to decontaminate water and wastewater by incorporating toxic (radioactive) metal cations and radionuclides such as ^{137}Cs and ^{90}Sr (e.g., Mumpton, 1999; Ghobarkar et al., 1999). Hydrated oxysalts with layered structures can be used for the immobilisation of toxic components migrating in urban and other waste dumps, such as Cr ions or halogens (Pöllmann, 1994a, b).

Still, each year huge amounts of waste containing toxic metal compounds (especially of As, Bi, Hg, Pb, Sb, Se, Tl, and radioactive elements) are produced in the form of smelter furnace wastes, galvanic sludges, incinerator ashes, red muds, flue-gas desulphurisation products, rests/byproducts of paint and pesticide production, et cetera. These wastes are difficult or impossible to economically recycle and to store safely.

Our condensed, up-to-date review will first briefly discuss the crystal chemistry of the crandallite, beudantite and alunite mineral groups, including new results from analyses of natural and synthetic members. This is followed by a summary of the widely varying types of natural occurrences, which will illustrate how the compounds act as natural reservoirs of toxic metals and barriers of their further spreading into the environment. Recent data on thermodynamic stability fields and the crystallography will also be addressed. Finally, current and possible uses are reported and the suitability for a long-term fixation of toxic metals is discussed by comparison with other, well-characterised storage minerals.

Crystal chemistry

Members of the crandallite, beudantite and alunite (jarosite) groups form part of the large supergroup of natural and synthetic compounds with the alunite-type structure. Their general formula is $AB_3(\text{XO}_4)_2(\text{OH,H}_2\text{O})_6$, where A =monovalent (H_3O , Na, K, Rb, Ag, Tl, ...), divalent (Ca, Sr, Ba, Pb, Hg, ...), trivalent (Bi, rare earth element=REE) or

tetravalent cation (Th, Zr), B =trivalent cation (Al, Fe, Cr, ...) and minor Cu^{2+} , Zn^{2+} , Sb^{5+} , Nb^{5+} , Ta^{5+} , and X = P^{5+} , As^{5+} , S^{6+} , Se^{6+} , Cr^{6+} and minor Si^{4+} (Hintze, 1933; Palache et al., 1951; Dutrizac et al., 1981; Jambor and Dutrizac, 1985; Lottermoser, 1990; Schwab et al., 1990; Lengauer et al., 1994; Mandarino, 1999; Kolitsch et al., 1999a). The hydroxyl group in the formula can be replaced by minor amounts of Cl^- and F^- . Typical examples are alunite, $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$, jarosite, $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$, beudantite, $\text{PbFe}_3(\text{AsO}_4)_2(\text{OH,H}_2\text{O})_6$, dussertite, $\text{BaFe}_3(\text{AsO}_4)_2(\text{OH,H}_2\text{O})_6$, crandallite, $\text{CaAl}_3(\text{PO}_4)_2(\text{OH,H}_2\text{O})_6$, plumbogummite, $\text{PbAl}_3(\text{PO}_4)_2(\text{OH,H}_2\text{O})_6$, synthetic $\text{Hg}_{0.5}\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$, synthetic, $\text{NaAl}_3(\text{CrO}_4)_2(\text{OH})_6$ and synthetic, $\text{KCr}_3(\text{SO}_4)_2(\text{OH})_6$. Pronounced solid solubility phenomena are widespread in natural samples (e.g., Wise, 1975; Scott, 1987; Rattray et al., 1996; Birch and van der Heyden, 1997; Hochleitner and Fehr, 1996; Jambor, 2000; Scott, 2000). Different and contradictory nomenclatory schemes for the naturally occurring compounds have been developed (Scott, 1987; Novák et al., 1994) and an improvement of the current, insufficient nomenclature has recently been proposed by Jambor (1999). The suggested improvement was the subject of further discussion (Jambor, 2000; Scott, 2000).

Unusual elements in alunite-type compounds

New chemical-analytical data on natural and synthetic members demonstrate that several elements can be incorporated into the alunite-type structure which were previously unknown to show such behaviour. The elements currently known to occur in non-negligible amounts in alunite-type compounds are listed in Table 1.

The work of Kolitsch et al. (1999a) on an Sb-rich variety of dussertite, the Ba-Fe-arsenate member of the crandallite group, suggests that, contrary to previous ideas, the structure type may accommodate significant amounts of Sb^{5+} , which is substituting for cations on the B site, but not for As^{5+} on the X site. Small, but distinct contents of Sb have also been found in the Pb-members beudantite and segnitite (Kolitsch, 1999). An Sb-bearing Pb-Fe-arsenate member additionally contained very small amounts of W^{6+} (Kolitsch, unpublished semiquantitative EDS analyses), which is assumed to replace the Fe^{3+} on the B site, as was shown for other ferric iron minerals (Kolitsch, 1998).

Considerable amounts of chromium (6.3 wt.% CrO_3) have been found in the natural Pb-member philipsbornite by Walenta et al. (1982), who assumed

Table 1. Cations occurring in natural and synthetic alunite-type compounds (arranged in order of increasing cation valency; cations most dominant in minerals are underlined)

<i>A</i>	<i>B</i>	<i>X</i>
H ₃ O ⁺	Cu ²⁺ (minor)	Si ⁴⁺ (minor)
NH ₄ ⁺	Zn ²⁺ (minor)	C ⁴⁺ ¹²⁾
<u>Na</u> ⁺	Co ²⁺³⁾	
<u>K</u> ⁺	Ni ²⁺³⁾	<u>As</u> ⁵⁺
Rb ⁺	Mg ²⁺³⁾	<u>P</u> ⁵⁺
Tl ⁺	Mn ²⁺³⁾	
Ag ⁺		<u>S</u> ⁶⁺
	<u>Al</u> ³⁺	Se ⁶⁺¹³⁾
<u>Ca</u> ²⁺	<u>Fe</u> ³⁺	Cr ⁶⁺¹⁴⁾
<u>Sr</u> ²⁺	Cr ³⁺⁴⁾	
<u>Ba</u> ²⁺	Ga ³⁺⁵⁾	
<u>Pb</u> ²⁺	In ³⁺⁶⁾	
Hg ²⁺	V ³⁺⁷⁾	
Bi ³⁺	Ge ⁴⁺⁸⁾	
<u>LREE</u> ³⁺¹⁾		
	Sb ⁵⁺⁹⁾ (minor)	
Th ⁴⁺ , U ⁴⁺ , Zr ⁴⁺²⁾ (minor)	Nb ⁵⁺ , Ta ⁵⁺¹⁰⁾ (minor)	
	W ⁶⁺¹¹⁾ (minor)	

Note: References for most of the individual compounds are given in Lengauer et al. (1994) and in the text of the present work. Specific references are: ¹⁾ LREE = light rare earth elements; the presence of some Sm²⁺ on the *A* site has been proposed by Mordberg et al. (2000); ²⁾ Landa et al. (1995); ³⁾ Typical jarosite wastes from zinc hydrometallurgical processes also contain minor Mg and Mn, and traces of Cd according to Simoncini et al. (1997), but confirmation is required; concerning Cd behaviour see also text. Very minor Co, Ni and Mn can be incorporated in synthetic plumbojarosite (Dutrizac and Dinardo, 1983); ⁴⁾ Lengauer et al. (1994); Johan et al. (1995); Bottrill (pers. comm., 1998) (see text); ⁵⁾ Tananaev et al. (1967a, b), Dutrizac (1984), Bernstein (1986), Kamoun et al. (1989), Jambor et al. (1996), Dutrizac and Chen (2000); ⁶⁾ Dutrizac (1984), Dutrizac and Dou Mingmin (1993); ⁷⁾ Kolitsch et al. (1999c) and references therein; ⁸⁾ Jambor et al. (1996) (see text for discussion); ⁹⁾ Kolitsch (1999); Kolitsch et al. (1999a); ¹⁰⁾ Lottermoser (1990); ¹¹⁾ Kolitsch (unpublished semiquantitative EDS analyses; see text); ¹²⁾ questionable according to Jambor (1999); ¹³⁾ Leclerc (1980), Dutrizac et al. (1981), Dutrizac (1984), Breitingner et al. (1997); ¹⁴⁾ Cudennec and Bonnin (1977), Dutrizac (1984).

that the Cr substitutes for As and S and suggested that the *X* site in the *XO*₄ group is occupied by (As_{1.57}Cr_{0.40}S_{0.10})_{Σ2.07}. However, according to recent analyses of other philipsbornite samples containing considerable Cr, there is strong evidence that Cr is present as Cr³⁺ and substitutes Al by up to 50 at.% (Bottrill, pers. comm.). Up to 18% Cr³⁺ on the *B* site

have been reported in natural gorceixite (Johan et al., 1995). Trace amounts of Cr have also been detected in a natural plumbojarosite (Pring et al., 2000). Although no alunite-type chromate end members are known in natural environments, synthetic chromate members have been reported (see Lengauer et al., 1994).

Other rare and unusual elements have also been reported recently in alunite-type minerals. A Se-rich, beudantite-related Pb-Fe-arsenate-sulphate member from a Se-rich deposit (Baccu Locci mine, Sardinia; Gramaccioli et al., 1997) has been identified recently (Kolitsch, unpublished semiquantitative EDS analyses and X-ray powder diffraction data). A sample of a natural Pb-member, beudantite, from a Czech locality contained In, substituting for Fe, in the range of 1–3 wt.% (Sejkora, pers. comm.). Synthetic In³⁺-members have also been reported and a complete solid solution between NaIn₃(SO₄)₂(OH)₆ and NaFe₃(SO₄)₂(OH,H₂O)₆ was observed (Dutrizac and Dou Mingmin, 1993). Trivalent gallium ions are dominant on the *B* site in gallobeudantite, PbGa₃(AsO₄,SO₄)(OH,H₂O)₆, and other Ga-dominant members have been identified in the gallobeudantite-bearing assemblage as part of complex chemically zoned crystals (Jambor et al., 1996). Gallium was also found to be concentrated in jarosite and limonite as result of a study on the distribution of Ga and Ge in the oxidation zone of a sulphide deposit (Bernstein, 1986). Synthetic Ga³⁺-sulphate members have been prepared by Tananaev et al. (1967a, b) and Dutrizac (1984), and complete solid solubility between *M*Ga₃(SO₄)₂(OH)₆ and *M*Fe₃(SO₄)₂(OH,H₂O)₆ (where *M* = Na, K or NH₄) was demonstrated (Kamoun et al., 1989; Dutrizac and Chen, 2000). Interestingly, the gallobeudantite mentioned above was also found to be Ge-bearing, and Jambor et al. (1996) suggest the Ge⁴⁺ to substitute for the octahedrally coordinated Ga³⁺. However, as Ge⁴⁺ can occur in both 4- and 6-fold coordination, it could also substitute for the As/S (a similar behaviour is known from Si which is commonly found in very small amounts in phosphate and arsenate members). Small amounts of Nb⁵⁺ and Ta⁵⁺ on the *B* site were detected in crandallite-group minerals from rare-earth ore deposits (Lottermoser, 1990). The first naturally occurring V³⁺-dominant member of the alunite supergroup, springcreekite [Ba(V³⁺,Fe³⁺)₃(PO₄)₂(OH,H₂O)₆], has been described recently (Kolitsch et al., 1999c). In natural gorceixite, BaAl₃(PO₄)₂(OH,H₂O)₆, a considerable substitution of V³⁺ for Al³⁺ has been reported (Johan et al., 1995). No vanadates with the alunite-type structure are known, a fact which may be explained by the too large size of the V⁵⁺ ion for the *X* site.

Recent analyses of natural Pb-members from an unusual assemblage of Cd-bearing secondary minerals from Broken Hill, New South Wales, Australia, demonstrate that these Pb-members do not incorporate the toxic Cd (Kolitsch et al., in prep.). This confirms laboratory studies demonstrating that Cd^{2+} is not selectively adsorbed onto or incorporated in the (pure sulphate) jarosite phase (Dutrizac and Weatherell, 1989; Dutrizac et al., 1996), and that only very small amounts of Cd may be incorporated into hydrometallurgically precipitated jarosites (Simoncini et al., 1997).

In summary, Table I shows that the title compounds can incorporate the following large number of toxic or radioactive metals: Tl, Sr, Pb, Hg, Bi, REE, Th, Cr, Se, Sb, As. They may also be able to fixate U, although this is yet to be established. On the other hand, the alunite-type does not seem to be able to incorporate the toxic Cd or radioactive isotopes of the very large Cs (Dutrizac and Jambor, 1987a). The synthesis of chemically pure Hg jarosite would be very difficult, however, as the compound is stable only in a very narrow pH range; Hg jarosite has also not yet been found in nature (Dutrizac and Chen, 1981).

Occurrences and thermodynamic stabilities

Alunite-type sulphates, phosphates and arsenates are widespread in a very large variety of natural geological environments. As stable weathering products of the rock-forming minerals monazite and apatite, phosphates of the crandallite group are common forms of terrestrial soil and sediment phosphate (Norris, 1968; Nriagu, 1984). In these soils the minerals often contain high amounts of trace elements such as Pb, Cu, Cr, etc. (Norris, 1968). Lead arsenate-sulphates were also noted in arsenic-rich soils (e.g., Presant and Tupper, 1966). Other occurrences were recorded in medium-grade metamorphic rocks, hydrothermal veins, greisens, pegmatites, bauxites and laterites, coals and carbonatites, as well as placer deposits and marine sandstones (e.g., Spötl, 1990; Morteani and Ackermann, 1996; Rasmussen, 1996; Rasmussen et al., 1998; Baldwin et al., 2000). Heavy metal phosphate, arsenate and sulphate members are common as secondary minerals in the oxidised zones and gossans of ore deposits, where they limit the further migration of heavy metal ions (e.g., Scott, 1987; Birch and van der Heyden, 1997; Levy et al., 1997; Kolitsch and Elliott, 1999). Sulphate members commonly occur in acid mine-drainage (e.g., Alpers et al., 1994), and it is known that jarosite compounds quickly crystallise wherever highly acidic, naturally formed or anthropogenic aqueous solutions are present in areas of

active or abandoned mining of Fe-bearing sulphide ores (e.g., Alpers et al., 1989; Lin and Herbert, 1997). Numerous investigations showed that these compounds readily incorporate a large range of different metal impurities. Tl-, Pb-, As-bearing and -fixating jarosite has been observed as a secondary, anthropogenic compound in dumps of roasted pyrite ores (Bambauer et al., 1987). The preferred incorporation of Tl in jarosite (and iron oxide) under processes of extreme oxidation and acid leaching has also been reported from a natural occurrence (Scorgie, 1991).

In mining-related acidic lakes, dense crusts of jarosites can serve as a natural self-seal (Schuiling and Van Gaans, 1997). Jarosite waste was produced in a smelter in Australia since 1973 and shipped to a government chosen ocean disposal site. It did not cause any harmful effects on the environment, as extensive monitoring and investigation for over 20 years, including sediment and fish surveys, have demonstrated (Sanderson and Wilson, 1994). Anthropogenic lead phosphate members are found in the vicinity of roads and highways where they form from leaded petrol consumed by automobiles. In these occurrences the compounds serve as a naturally formed host for toxic Pb, therefore reducing the output and spread of anthropogenic Pb into ecosystems (Nriagu, 1984; Eighmy et al., 1999; Morin et al., 2001).

As shown by the wide variety of geological occurrences, some of the title compounds can form at temperatures as low as $\sim 10^\circ\text{C}$ and some are stable up to about 500°C . Observed and deduced pH values for conditions of formation range between <1 and 10 . The compounds form under strongly oxidising to (rarely) slightly reducing conditions. Laboratory studies have shown that both phosphate and arsenate members of the crandallite group exhibit extremely low solubilities (Norris, 1968; Schwab et al., 1993; Roca et al., 1999), with the arsenates being thermodynamically more stable. Crandallite itself, previously considered to be stable only in the presence of impurities (Schwab et al., 1990), has been shown to be a stable phase in the system $\text{CaO-Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ at 200°C (Yuh and Rockett, 1981). The relative stabilities of various alkali jarosites were investigated by Dutrizac (1983) who demonstrated that jarosite, $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$, is the most stable among these. Thermodynamically stable, pure synthetic alkali jarosites can incorporate an only very limited amount of arsenate substituting for sulphate (Dutrizac and Jambor, 1987b).

Thermodynamic data are comparatively scarce, however, and stability fields of only few alunite-type minerals have been evaluated (Brown, 1971; Hladky

and Slansky, 1981; Yuh and Rockett, 1981; Stoffregen and Cygan, 1990, and references cited therein; Baron and Palmer, 1996a, b).

Several theoretical end members (such as, for instance, the Ba-Fe- and Ca-Fe-phosphate representatives) do not seem to be stable, probably caused by unfavourable size relationships between the constituent *A*, *B* and *X* cations. The pure theoretical end member $\text{Pb}_{0.5}\square_{0.5}\text{Al}_3(\text{SO}_4)_2(\text{OH})_6$ is unknown from geologic environments, although synthetic $\text{Pb}_{0.5}\square_{0.5}\text{Al}_3(\text{SO}_4)_2(\text{OH})_6$ has been prepared in an autoclave using a hydrothermal technique (Okada et al., 1987), indicating that this compound may be stable only at elevated pressures. The related alunite-type Pb-sulphate osarizawaite, $\sim \text{Pb}(\text{Al}, \text{Cu})_3(\text{SO}_4)_2(\text{OH})_6$ (with Al:Cu at least $\sim 2:1$, and some Al being replaced by Fe), may be considered a Cu(+Fe?)-stabilised variety of the pure Pb-Al-sulphate end member (see also Dutrizac, 1984; Jambor, 1999). It is predicted that more natural members of the alunite supergroup will be found in nature, particularly in geologically unusual environments.

Crystallography

Almost all of the members of the crandallite, beudantite and alunite groups crystallise in the rhombohedral space group $R\bar{3}m$ first established for alunite (Hendricks, 1937; Wang et al., 1965; Menchetti and Sabelli, 1976). The basic structure of an alunite-type compound $AB_3(XO_4)_2(\text{OH}, \text{H}_2\text{O})_6$ consists of sheets of corner-sharing BO_6 octahedra parallel to the basal pinacoid $\{0001\}$ (Fig. 1). Located in-between the sheets are small to very large, generally 12-coordinated *A* cations (e.g., Na, Ca, Pb, Hg), and the sheets themselves are corner-linked to XO_4 tetrahedra (Fig. 1). Hexagonal unit-cell parameters *a* and *c* lie in the ranges 6.97–7.44 and 16.2–17.8 Å, respectively (see also detailed listing of unit-cell data in Lengauer et al., 1994). Due to partial or complete ordering of divalent *A* cations, the *c* axes in some sulphate members are doubled (e.g., plumbojarosite, $\text{Pb}_{0.5}\square_{0.5}\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$). There is also a currently unique, unnamed natural phosphate member, $\text{PbFe}_3(\text{PO}_4)_2(\text{OH}, \text{H}_2\text{O})_6$, whose crystal structure exhibits a distortion at the Pb sites, leading to two independent Pb atoms in the structure, and a doubling of the *c* axis (Jambor, 1999, 2000).

Few exceptions are known, in which the symmetry of an alunite-type compound is or is assumed to be slightly lower than rhombohedral. This is most probably caused by a disordered or split arrangement of *A*-cations [disordered Ca in crandallite, Blount, 1974; Ba

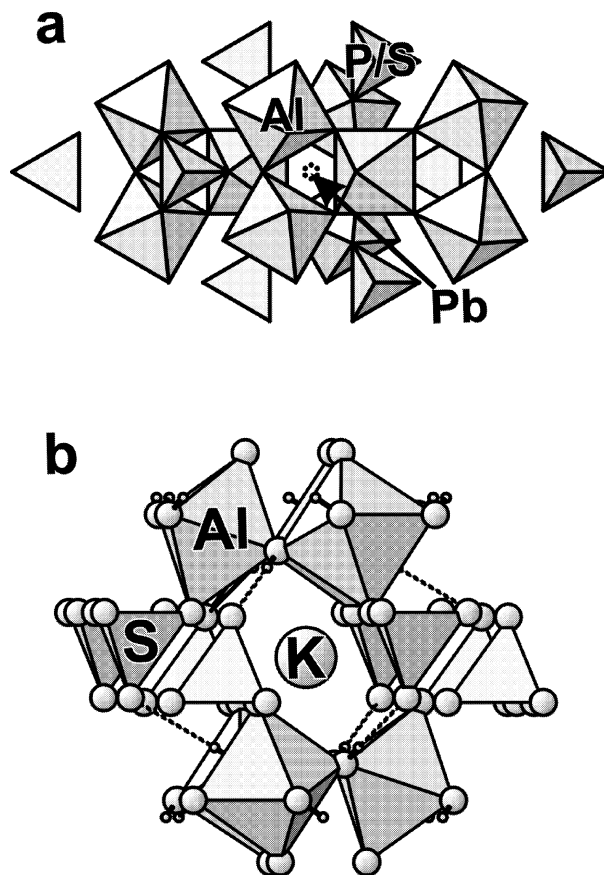


Figure 1. The alunite-type structure exemplified by the atomic arrangement of (a) hinsdalite, $\text{PbAl}_3[(\text{PO}_4, \text{SO}_4)]_2(\text{OH}, \text{H}_2\text{O})_6$, in a projection along the *c*-axis (Kolitsch et al., 1999b) (note that the Pb atom is disordered), and (b) alunite $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$ (Menchetti and Sabelli, 1976) projected approximately along the a_2 -axis and perpendicular to the *c*-axis; the H-bonding scheme is indicated with dashed lines between H atoms (small spheres) and O atoms (medium-large spheres). ATOMS drawings (Shape Software, 1999).

in monoclinic gorceixite (space group *Cm*), Radoslovich and Slade, 1980; Radoslovich, 1982; Blanchard, 1989; K in monoclinic jarosite (space group $C2/m$), Göttlicher and Gasharova, 1999; disordered Na in natrojarosite, Gasharova et al., 2000; see also Kolitsch et al., 1999a]. Symmetry reduction has also been observed in several Pb-members, in which the reduction is due to the off-centre position of the Pb^{2+} ion caused by its $6s^2$ lone pair of electrons (for details see Kolitsch et al., 1999b, and references cited therein). Recently, Hochleitner and Fehr (1998) and Fehr et al. (2000) investigated the Pb-members plumbojarosite, $\text{Pb}_{0.5}\square_{0.5}\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$, and beudantite $\text{PbFe}_3[(\text{AsO}_4, \text{SO}_4)]_2(\text{OH}, \text{H}_2\text{O})_6$, by Mössbauer spectroscopy and found indications for the presence of two different Fe^{3+} positions. This observation corresponds with Raman spectroscopical data of Sasaki et al. (1998) who reported the presence of two

different SO_4^{2-} positions in plumbojarosite, one adjacent to Pb^{2+} and the other adjacent to the vacancy.

Other indications for small deviations from perfect rhombohedral symmetry in investigated samples are suggested by a fairly large number of reports on anomalous biaxial optics (e.g., Hintze, 1933; Palache et al., 1951; Walenta, 1966; Szymański, 1985). Some of these inferred very small deviations from rhombohedral (hexagonal) symmetry are obviously not detectable by X-ray methods. Strain due to inhomogeneous chemical compositions (often encountered in alunite-type minerals) probably plays an important role in reducing the symmetry (cf. Foord and Mills, 1978). The anomalies may be caused by very small deviations of metal and oxygen atoms from their ideal positions, or by ordering of hydroxyl ions and water molecules. Precession photographs of a sulphate-rich, optically distinctly biaxial negative benuaite, $\text{SrFe}_3[(\text{PO}_4, \text{SO}_4)]_2(\text{OH}, \text{H}_2\text{O})_6$, gave sharp diffraction patterns with a perfectly hexagonal symmetry, suggesting that the dominant scattering components in the investigated crystal occupy their ideal positions (Kolitsch, in prep.). Strong evidence for monoclinic symmetry of a synthetic jarosite prepared at 200°C has been given by Göttlicher and Gasharova (1999), based on the observation of split reflections in X-ray powder diffraction patterns and a single-crystal structure refinement, which indicated space group $C2/m$.

A disordered distribution of cations is firmly established for the *B* site (disordered Al^{3+} , Fe^{3+} and Cu^{2+} in osarizawaite; Giuseppetti and Tadini, 1980). A recent refinement of the structure of an Sb-rich dussertite, $\text{Ba}(\text{Fe}^{3+}_{0.84}, \text{Sb}^{5+}_{0.16})_3(\text{AsO}_4)_2(\text{OH}, \text{H}_2\text{O})_6$, shows that Fe^{3+} and Sb^{5+} are also completely disordered on their shared site (Kolitsch et al., 1999a). Disorder of V^{3+} and Fe^{3+} on the *B* site has been found in the new crandallite-group member springcreekite, $\text{Ba}(\text{V}^{3+}, \text{Fe}^{3+})_3(\text{PO}_4)_2(\text{OH}, \text{H}_2\text{O})_6$ (Kolitsch et al., 1999c).

Disorder on the *X* site has been observed for various mixed P/As/S-members (e.g., Kato and Miura, 1977; Szymański, 1988; Giuseppetti and Tadini, 1989; Kharisun et al., 1997; Kolitsch et al., 1999b). Reported ordering of P/S in corkite, leading to the non-centrosymmetric space group $R3m$ (Giuseppetti and Tadini, 1987), is considered doubtful (for discussions, see Kharisun et al., 1997, Kolitsch et al., 1999b). Obvious ordering of As/S has been reported for gallobendantite which was also attributed space group $R3m$ (Jambor et al., 1996).

Transmission electron microscope (TEM) studies, involving selected area electron diffraction (SAED), of a hinsdalite (Kolitsch et al., 1999b), an arsenatian corkite,

an arsenatian plumbojarosite and a synthetic thallium jarosite (Kolitsch, unpublished results) showed that all investigated samples give sharp reflection spots. No superstructures or deviations from the reported symmetries were observed within error limits.

No information is available on the exact nature of the disorder on the *B* and *X* sites. However, statistical disorder is highly probable as the *B* and *X* cations are tightly bonded to oxygen atoms. The possibility of dynamical disorder can not be excluded for some of the hydrogen atoms. Neutron diffraction or specialised spectroscopic methods may be useful to shed more light on disorder and possible local, short-range ordering. Although neutron diffraction studies were conducted on jarosite compounds they focused on the magnetic properties at very low temperatures (Inami et al., 1998), or on the localisation of H atoms, the nature of the H bonds and the content of oxonium cations (Schukow et al., 1999; investigation of synthetic alunites).

Various spectroscopic methods used to characterise alunite-type compounds (mostly sulphates) comprise infrared spectroscopy (e.g., Adler and Kerr, 1965; Rossman, 1976; Arkhipenko and Bokii, 1979; Serna et al., 1986; Breitingner et al., 1997, 1999), Raman spectroscopy (Serna et al., 1986; Breitingner et al., 1997; Sasaki et al., 1998; Gasharova et al., 2000), Mössbauer spectroscopy (e.g., Afanasev et al., 1974; Leclerc, 1980; Lakshmi Reddy et al., 1991; Vedanand et al., 1992; Hochleitner and Fehr, 1998, Fehr et al., 2000), magnetic susceptibility studies (e.g., Rossman, 1976; Harrison et al., 1997; Earle et al., 1999), and nuclear magnetic resonance spectroscopy (Bleam et al., 1989) as well as optical absorption and electron paramagnetic resonance spectroscopy (Rossman, 1976; Lakshmi Reddy et al., 1991; Vedanand et al., 1992). The cited authors predominantly investigated the local environment and site symmetry of atoms or polyhedra in their samples.

Current and suggested use of alunite-type compounds

Current use of alunite-type compounds is restricted. After heat treatment, Ca- and Sr-phosphates are used as fertilisers (Gilkes and Palmer, 1983). All natural compounds can be used as indicator minerals in exploration (e.g., Nriagu, 1984). High proton conductivity at ambient temperature has been found in hydrated pressed discs of hydronium alunite, $(\text{H}_3\text{O})\text{Al}_3(\text{SO}_4)_2(\text{OH})_6$ (Wing et al., 1980). In hydrometallurgical processes developed in zinc and nonferrous hydrometallurgical plants of the zinc industry, controlled precipitation of jarosite-type compounds is widely used to remove unwanted iron and heavy metal ions (e.g., Dutrizac and Kaiman, 1976;

Dutrizac, 1984). Detailed laboratory-scale studies of these processes have been conducted (e.g., Dutrizac, 1983; Jambor and Dutrizac 1983; Dutrizac, 1984). It was demonstrated, for example, that thallium preferentially enters the structure of jarosite by comparison to sodium and ammonium (Dutrizac, 1997), in agreement with data from natural environments (see above); therefore, jarosite precipitation provides an effective means of eliminating thallium from zinc (and possibly other) processing circuits. The natural Tl-dominant end member is known from a Tl-As deposit ($\text{Tl}_{0.8}\text{K}_{0.2}\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$, Balić Žunić et al., 1994). The chromate analogue of jarosite, on account of its high thermodynamic stability, may be used to remove Cr(aq) from chromium-contaminated water resources (Baron and Palmer, 1996b).

A novel technique for treating and recycling hydrometallurgical jarosite wastes has been reported recently by Simoncini et al. (1997). The technique is based on self-propagating reactions within a mixture of the jarosite waste materials and added aluminium and ferric oxide. Industrial jarosite waste arising from the hydrometallurgical processing of zinc-rich ores can also be recycled, resulting in Fe-rich glasses and glass-ceramics (e.g., Karamanov et al. 1999). Further use of these wastes is made by the production of new construction materials (Mymrin and Vazquez Vaamonde, 1999).

Crandallite group minerals were recently shown to be suitable for the safe incorporation of radioactive fission products (Ballhorn et al., 1989). This suitability had previously been suggested (Fron del, 1958), and it is also indicated by the crystal-chemical behaviour and long-term stability of natural REE phosphate members in uranium deposits, where they preferentially incorporated fission products (light REE, Zr) from natural nuclear reactor zones and limited their migration (e.g., Janeczek and Ewing, 1996; Dymkov et al., 1997; Gorshkov and Artyukhina, 1997). Landa et al. (1995) showed that, when jarosite was precipitated in the presence of trace amounts of thorium, a significant amount of thorium ('78%') was incorporated in the precipitate. Crandallite-type compounds are easily synthesised and very efficient in separating cations, especially radioactive ones, from aqueous solutions (patent by Brunner et al., 1987).

Advantages of alunite-type compounds

The outstanding crystal-chemical flexibility of the alunite structure allows a large variety of elements with very different sizes and valencies to be incorporated, as already reported by us earlier (Kolitsch and Pring, 1998).

Furthermore, complete or extensive solid solubility among end members is widespread and pronounced disorder of cations on the *A*, *B* and *X* sites facilitates the combined incorporation of different elements (metals). Accordingly, one could describe the alunite structure type as a "garbage-can" structure type, similar to the apatite structure type. Unlike "established" waste storage materials with the apatite-type structure, alunite-type compounds are able to incorporate Sb. On the other hand, the apatite structure can host about 50 different elements (e.g., Roy et al., 1978).

Relatively high thermodynamic stability up to 400–500°C and good chemical resistance over a large range of pH conditions have been established for the majority of the alunite-type compounds. Pb-members such as plumbogummite are especially stable (Schwab et al., 1993) and phosphate and arsenate members have very low solubilities. By contrast with apatite, the Ca-phosphate member crandallite is insoluble under neutral and alkaline conditions and cation exchange is only possible on surface positions (Fron del, 1958). The preparation of crandallite-type compounds by hydrothermal methods is fairly easy (e.g., Brunner et al., 1987; Ballhorn et al., 1989; Schwab et al., 1990). Numerous publications on natural occurrences of phosphate and arsenate members show that these readily form pseudomorphs after lead members of the apatite group. Therefore, they might be considered as a waste form possibly comparable or superior to apatites.

Interestingly, there exists a close relation between the alunite and the pyrochlore structure types (Goreaud and Raveau, 1980). Some of a large number of compounds with the pyrochlore structure have been used as storage materials for the incorporation of certain heavy metals (see Introduction). It is also worth noting that the alunite structure is strongly related to that of the Ca-Fe-phosphate mitridatite (Moore, 1974; Moore and Araki, 1977).

An obvious disadvantage of (Al- and Fe-dominant) alunite-type compounds are the relatively low waste-loading factors imposed by the stoichiometry. Nonetheless, components which would have to be added to produce a final waste storage material, are cheap (e.g., Fe- and Al-bearing precursor materials or solutions). The thermal stability does not exceed temperatures of approximately 400–500°C and is therefore lower than that of "established" storage materials such as apatites or perovskites. However, temperatures in either over- or underground toxic metal waste-dump sites would be well below 150°C.

Conclusions

Members of the crandallite, beudantite and crandallite groups are suggested to have great potential as stable and reliable hosts for toxic metals, on account of their high crystal-chemical variability, general stability and easiness of formation and preparation. Their potential in safely incorporating toxic metals is considered comparable to that of other well-characterised host structures (apatite, perovskite, pyrochlore).

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