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combined with a crystallographic phase transition. Similar mixed-valence states of iron have been observed by the Mössbauer effect in many other minerals: deerite, vonsenite, aegirine-augite, melonjosephite, and lipscombite.

3.1.4 Mössbauer Spectroscopy of Sn, Sb, Eu, Au

F.C. HAWTHORNE

Although ^{57}Fe work has dominated Mössbauer spectroscopy of minerals and other geological materials, there has been a small amount of work on other Mössbauer-sensitive nuclei. Of particular interest in this regard are ^{119}Sn, ^{121}Sb, ^{151}Eu, and ^{197}Au. Work on these species has been of considerable importance as it has provided some of the first direct information as to the valence states of these species in minerals.

^{119}Sn

Tin may be divalent ($5s^2 5p^0$) or quadrivalent ($5s^0 5p^0$) in minerals. In some tin minerals, the valence state is fixed by stoichiometry (e.g., cassiterite, $Sn^{4+}O_2$), whereas in other more complex minerals, the situation is less straightforward.

Sn has been detected in minor quantities in some garnets. The Mössbauer spectrum (Fig. 30a) looks like a singlet, but is a poorly resolved doublet. The IS value is 0.0 mm/s relative to cassiterite, showing the Sn to be quadrivalent, Sn^{4+}; in addition, the very small QS is consonant with very regular octahedral coordination, as expected if Sn^{4+} occupies the [Y] site in the garnet structure.

Sn is a common constituent in complex sulfosalt minerals, and because of the multiplicity of cations with possible variable valence states, it is important that the cation valences be characterized as their roles in the structure(s) are very sensitive to differences in valence state. Franckeite, ideally $Pb_5FeSn_3Sb_2S_{14}$, shows considerable chemical variability, with solid solution towards incaite, essentially a Ag- and Sn-rich franckeite. The ^{119}Sn spectrum of near end-member franckeite shows a strong singlet due to Sn^{4+} and a weak doublet due to Sn^{2+} (Fig. 30b). In incaite (Fig. 30c), the Sn^{2+} doublet has greatly increased in intensity relative to the Sn^{4+} peak, showing that the substitution $Sn^{2+} \rightleftharpoons Pb^{2+}$ is an important aspect of this sulfosalt series.

^{121}Sb

Antimony may be trivalent ($5s^2 5p^0$) or pentavalent ($5s^0 5p^0$) in minerals, and its role in the structure is sensitive to its valence state.

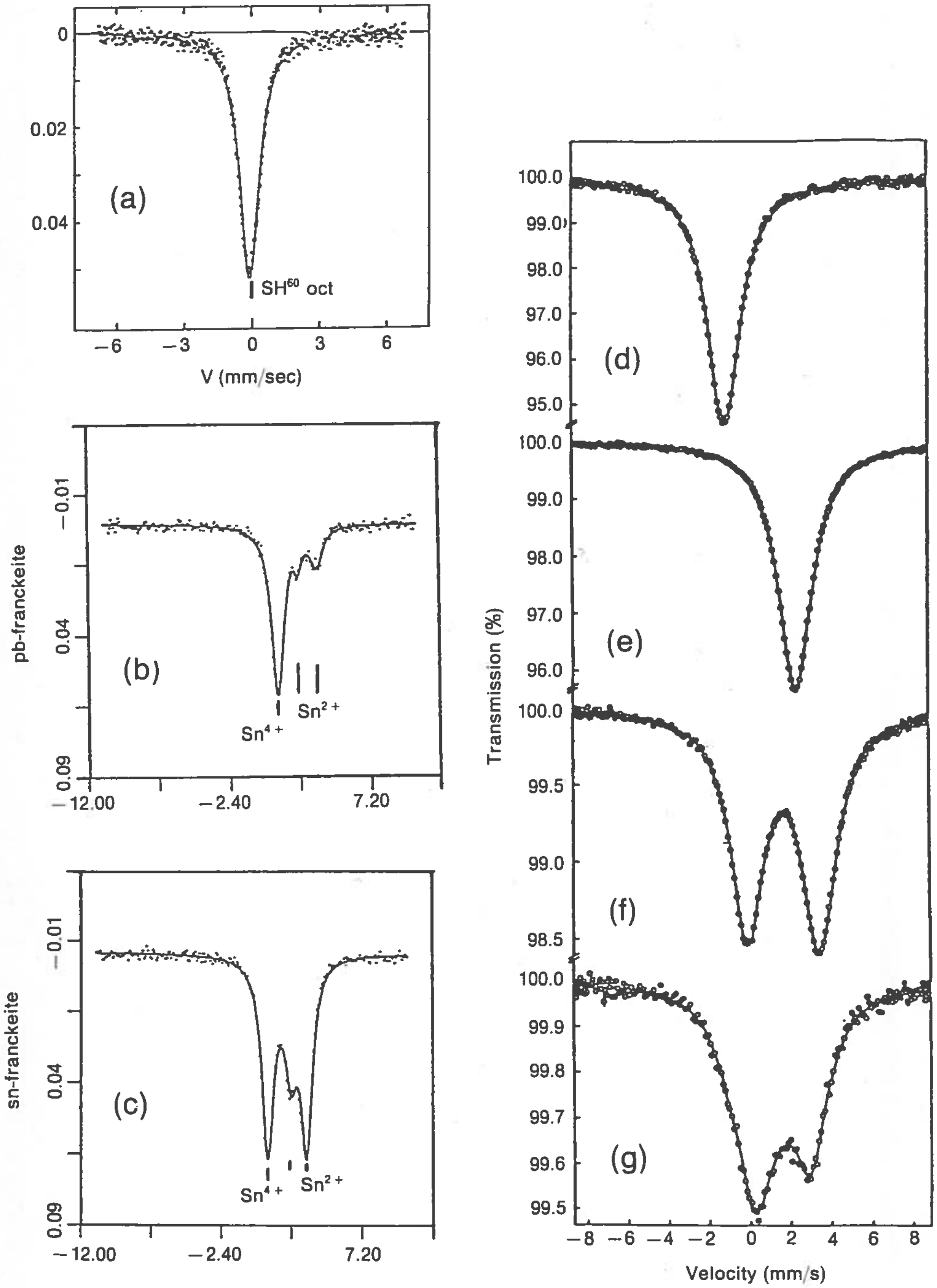

Fig. 30a–g. Mössbauer spectra of: **a** ^{119}Sn in garnet; **b** ^{119}Sn in (Pb-rich) franckeite; **c** ^{119}Sn in incaite (Sn-rich franckeite); **d** ^{197}Au in native gold; **e** ^{197}Au in aurostibite ($AuSb_2$); **f** ^{197}Au in nagyagite [$Pb_5Au(Te,Sb)_4S_5$]; **g** ^{197}Au in sylvanite ($AuAgTe_4$). (After Amthauer et al. 1979)

Antimony is pentavalent in ordonezite, $ZnSb_2^{5+}O_6$, as indicated by the electroneutrality principle. The Mössbauer spectrum shows a single line (actually a poorly resolved quadrupole-split octuplet) with an IS of 9.1 mm/s, diagnostic of Sb^{5+}. In franckeite, the situation was not clearcut because of the possible variable valences of Sn, Sb and Fe. However, the spectrum showed a single line with an IS of − 13.7 mm/s, diagnostic of Sb^{3+}.

^{151}Eu

Europium may be divalent or trivalent in minerals; it is usually (assumed to be) trivalent, but the geochemical Eu anomaly common in many rocks has been explained as the substitution of Eu^{2+} for Ca in plagioclase feldspars. Synthesis of Eu-bearing anorthite showed the Eu was divalent in the feldspar, the first direct conformation of this important point.

^{197}Au

Gold may be metallic, monovalent, or trivalent. However, the IS values do not reliably distinguish between these different valence states (Fig. 24a), and a consistent interpretation of the spectra of gold minerals has not yet been advanced.

The spectra of several gold minerals are shown in Fig. 30. Native gold gives a singlet with an IS of − 1.23 mm/s (relative to the Pt source); alloying with silver gradually increases the isomer shift which can reach values of 1.0 mm/s for dilute gold in a silver matrix. Aurostibite, $AuSb_2$, is cubic and has the pyrite structure. It gives a singlet with a large positive IS. Nagyagite, $Pb_5Au(Te,Sb)_4S_5$, gives a doublet, presumably the result of quadrupole-splitting, with a large positive IS. Sylvanite, $AuAgTe_4$, is monoclinic and gives a significantly more complicated spectrum consisting of (at least) two quadrupole-split doublets with very different IS and QS values.

Mössbauer spectroscopy has been used effectively in the characterization of gold ores, and to follow the progress of gold extraction in the smelting and roasting processes used in commercial gold recovery.

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