

EXAFS AND XANES STUDIES OF GERMANIUM
IN SOME MINERALS AND RELATED SUBSTANCES

BERNSTEIN, Lawrence R., 380 Willow Road, Menlo Park, CA 94025 USA; WAYCHUNAS, Glenn A., Center for Materials Research, Stanford University, Stanford, CA 94305 USA

Germanium displays diverse geochemical behavior, being concentrated in such disparate materials as coal, iron meteorites, sphalerite deposits, copper sulfide deposits, and iron oxides and hydroxides (Bernstein, 1985). The recently opened Apex Mine in southwest Utah (Bernstein, 1986) extracts Ge from limonite, goethite, and hematite that contain as much as 0.7 wt. percent Ge, though the nature of the Ge in this material has remained unknown.

To gain a better understanding of the crystal and solution chemistry of Ge, high resolution EXAFS and XANES fluorescence spectra were obtained at the Stanford Synchrotron Radiation Laboratory (SSRL) on powdered samples and an aqueous solution.

Near-edge (XANES) spectra for several materials are shown in Figure 1. All of the spectra show a smooth, sharp initial edge, with no pre-edge features. The position of the edge crest appears to be most influenced by the type of ligand and the coordination number: highly covalently-bonded ligands (Ge,As,S,P) produce lower energies than more ionically-bonded ligands (O,OH), while tetrahedral coordination (GeO₂ with quartz structure, aqueous Ge, plus all the compounds in Figure 1a except GeS) produces lower energies than octahedral coordination (all the other compounds). In stottite, FeGe(OH)₆, octahedrally-coordinated hydroxyl groups produce the highest observed edge-crest energy.

Materials containing Ge in regular or nearly-regular octahedral coordination (stottite, hematite, limonite) have a distinct feature at about 11135 eV. In GeO₂ (rutile structure) and possibly in GeS, which both contain Ge in distorted octahedral coordination, this feature is split. Materials containing tetrahedrally coordinated Ge have one or more features at energies less than 11135 eV, apparently dependent upon the particular ligand.

The EXAFS results have led to several new conclusions. In particular: (1) Ge(IV) substitutes for Fe(III) in hematite and probably in limonite from the Apex Mine; (2) the dilute, neutral aqueous solution contains Ge chiefly as Ge(OH)₄; and (3) the Cu-Fe-Ge-As-Zn sulfides renierite and germanite contain Ge(IV) in regular or nearly regular tetrahedral coordination. In the germanian hematite from the Apex Mine (0.7 wt. percent Ge), six nearest-neighbor oxygen atoms are at about 1.87 Å, and 4 second-neighbor iron atoms are at about 2.90 Å; these figures conform well to the expected values for Ge(IV) in the octahedral Fe(III) crystallographic site of hematite.

References

- Bernstein, L.R. (1985) Germanium geochemistry and mineralogy. *Geochimica et Cosmochimica Acta*, v. 49, p. 2409-2422.
Bernstein, L.R. (1986) Geology and mineralogy of the Apex germanium-gallium mine, Washington County, Utah. U.S. Geological Survey Bulletin 1577, 9 p.

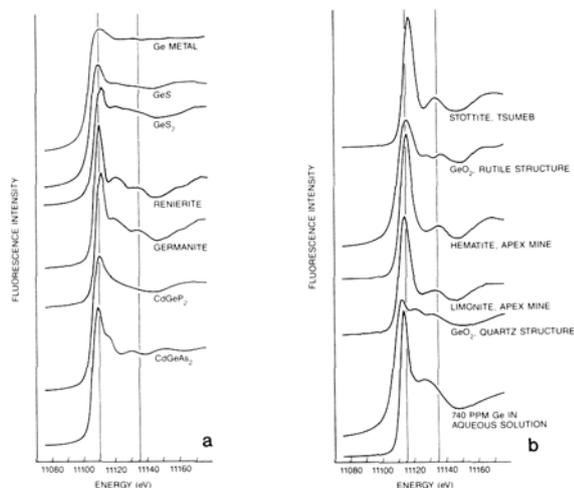


Figure 1. K-edge spectra for Ge.

THE CRYSTAL STRUCTURE OF GRISCHUNITE

BIANCHI, R., PILATI, T., C.N.R. Centre c/o Dept. of Physical Chemistry, University of Milan; MANNUCCI, G., Earth Science Dept., University of Milan, I-20133 Milan, Italy

On a fragment of type material, kindly supplied by Prof. S. Graeser, the structural determination of grischunite, a new arsenate mineral from Falotta, Graubünden, has been carried out by X-ray diffraction. The unit cell data $a=12.855(2)$, $b=13.497(2)$, $c=12.047(1)$ Å, space group $Pc\bar{a}b$, $Z=4$ are in agreement with the previously published data by Graeser et al. (1).

For determining and refining the structural data, of 2393 independent reflections which have been collected using a Nonius CAD-4 diffractometer, 1739 for which $I > \sigma(I)$ have been considered; an empirical absorption correction according to Walker and Stuart was also applied. The structure was solved by direct methods, using the MULTAN routine, and refined by least squares: the final R index is 0.036.

Of the three non-crystallographically equivalent sites containing transition metals, one has shorter distances with the adjacent O atoms (average 2.090(2) Å, against 2.189(2), and 2.230(2) Å, respectively). The Ca and Na atoms in the structure essentially occupy two additional (different) positions, with average Me-O distances 2.548 and 2.503 Å, respectively; for sodium, the equivalent B (1.89 Å² against 0.7 Å² for all the other metal atoms) indicates a partial occupancy of the Na site. All these reasons give evidence for changing the proposed formula (Ca,Na)(Mn²⁺,Fe³⁺)₂(AsO₄)₂ to a new one, i.e. NaCa₂Mn₂Fe³⁺(AsO₄)₆·2H₂O, with about one-half of Mn substituted by Fe in the position with short Me-O distances; the presence of water has also been ascertained by examining the difference Fourier map. The agreement with the analytical data reported by Graeser et al. (2) is improved, and the mineral seems to be more related to the alluaudites.

- (1) Graeser, S., Schwander, H., & Suhner, B., *Schweiz. min. petr. Mitt.* 64, 1-10 (1984)

• CHEMICAL MINERALOGY OF MARINE EVAPORITES

BILLO, S.M., Department of Geology, King Saud University, ad-Dir'iyah, Riyadh, Saudi Arabia

Quantitative studies on the course of crystallization during evaporation of sea water reveal that the sequence of deposition of early evaporite minerals consists of calcium carbonate, calcium sulfate, and halite, successively. The order of deposition depends on temperature, mineral solubilities, and concentration of the various ions. Most ancient marine evaporite deposits are mineralogically similar to the preceding sequence. The Permian Castile Formation in the Delaware Basin of Texas and New Mexico is a classic example of a totally interrupted marine evaporite sequence consisting of gypsum or anhydrite and halite with basal interlaminated carbonate layers. Recent studies on the mineralogy and trace element distribution of Castile evaporites using differential thermal analysis (DTA) and atomic absorption spectrophotometry, in addition to elaborate computer programming, have confirmed positive correlation with the established resolution of the type section of the Castile Formation into parallel and independent time-series of halite, calcium sulfate, calcium carbonate, organic matter, magnesium, strontium, potassium and iron for depicting the changing climatic patterns in the region.

ABSTRACTS with PROGRAM

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